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The Development of a Deployable Water Quality Monitoring System

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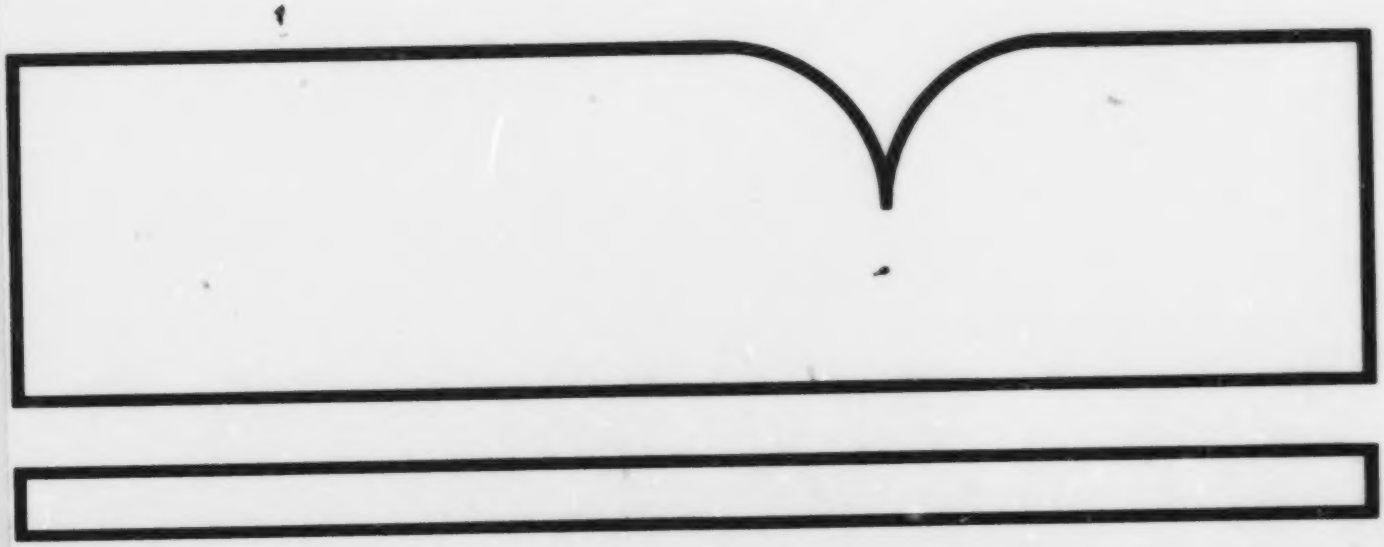

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The stability and accuracy of current off-the-shelf water quality sensors are evaluated. Biological fouling was deemed one of the most serious problems in nullifying sensor capability. Methods to reduce biofouling were evaluated. Of the potential measures to eliminate biofouling, the focal "kill-zone" approach appears to be most feasible and the simplest to implement.

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SUMMARY

The purpose of this project was to evaluate the stability and accuracy of off-the-shelf water quality sensors used for extended periods of time. The Hydrolab Surveyor Model 6D, Martek Mark IV and Ocean Data Model 101A probes were used in the test.

Based on an extensive literature survey and laboratory tests, biological fouling was deemed one of the most serious problems in nullifying sensor capability. Several possible methods to reduce biofouling include:

1. in situ ultrasonic cleaning of the probes
2. in situ generation of sodium hypochlorite from sea water
3. local application of heat
4. light-proof environment to suppress algae growth
5. generation of a local "kill zone" utilizing toxic antifouling paints
6. periodic injection of a biocide
7. incorporation of toxic compounds into dissolved oxygen membrane.

Of these seven potential measures to eliminate biofouling, the local "kill zone" approach appears to be the most feasible and simplest to implement. In field tests at Louisiana State University (LSU), it proved to be effective in controlling biological growths.

An experimental program was designed to evaluate probe performance under field conditions. Tests were conducted in a freshwater environment for several extended periods during which calibration procedures and the stability of calibration were studied. A statistical study of parameter variation is included.

Comparative results of the various probes are given for temperature, dissolved oxygen (DO), pH and conductivity for a 6-week test period in a freshwater environment.

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ABBREVIATIONS AND SYMBOLS

LSF	-- least squares fit
R^2	-- coefficient of determination
CI	-- confidence interval
DO	-- dissolved oxygen
pH	-- negative logarithm of the effective hydrogen-ion concentration
MK	-- Martek probe
HL	-- Hydrolab probe
OD	-- Ocean Data probe
NDP	-- number of data points used in statistical analysis
T	-- observed temperature
C	-- observed conductivity
T_r	-- reference temperature
C_r	-- reference conductivity
b	-- slope of least squares fitted curve
σ_b	-- standard deviation of slope

SECTION 1

INTRODUCTION

This research project was implemented to provide input data to a longer term effort aimed at developing a water quality monitoring system that can be remotely deployed up to 45 days.

The first phase of the research was devoted to a literature survey and the potential problems that may arise in deployable sensor design. Possible methods to alleviate these problems were reviewed. It was found that no large scale effort in the area of long-term monitoring with in situ sensors has been mounted, due primarily to the many problems that are encountered when probe packages are left unattended for extended periods of time.

The primary problems encountered are biological fouling and the lack of long-term stability of the sensors, with chemical and physical degradation contributing to a lesser extent.

Little can be done within the context of this project to combat chemical degradation (i.e., corrosion) since it would involve a redesign of the probes to eliminate those surfaces that are prone to corrosion or the design of new materials that are corrosion resistant. These are typical of tasks that would be undertaken in a longer-term program.

Physical degradation (i.e., collection of physical debris on the probe surfaces and within the cylindrical housings) can be significantly reduced by a redesign of the probe package to prevent foreign substances from coming into direct contact with the active probe surfaces.

Biological fouling (i.e., growth of organisms on the active probe surfaces) is the most serious problem and also the most difficult to combat. The literature search resulted in consideration of several possible methods to reduce biofouling: 1) in situ ultrasonic cleaning of the probes, 2) in situ generation of sodium hypochlorite from sea water, 3) local application of heat, 4) light-proofing the environment to suppress algae growth, 5) generation of a local "kill zone" using toxic antifouling paints, 6) periodic injection of a biocide, and 7) incorporation of toxic compounds into the dissolved oxygen membrane.

Of these seven potential measures to eliminate biofouling, the local "kill zone" approach appears to be the most feasible and simplest to implement. It requires a minimal increase in power requirements and has been proven effective in a limited number of field tests.

The test phase of the project was designed to determine the performance of off-the-shelf water quality sensors in a realistic aquatic environment for an extended period of time. Tests were accomplished without any adjustments to the sensors after initial calibration and deployment except with respect to the circulator on the dissolved oxygen sensor. In order to test the "kill zone" hypothesis, a container was designed to enclose one of the probe packages, and a circulating system was incorporated in the "new" system to periodically flush the container to bring a fresh water sample into contact with the probes. The inside of the container was coated with an antifouling paint that contained tributyltin fluoride as an active toxic agent. A long-term (6 to 8-weeks) test of the probe packages in a realistic aquatic environment was undertaken. These first tests were restricted to a fresh water site; future tests will be conducted in saline and brackish environments. Four water quality sensor probes (a Hydrolab Surveyor Model 6D, two Martek Mark IV and an Ocean Data Model 101A) were used in the field tests.

Upon completion of the field tests and calibration checks, the long-term probe performance was compared to simultaneous parameter measurements using laboratory standards. The long-term performance of the sensors enclosed in the toxin-coated container was compared to that of the other probes without the "kill zone."

A major aim of this project was to access the ability of these sensor packages to maintain calibration in a realistic aquatic environment.

It was determined that both environmental degradation and the lack of long-term stability of the sensors are major factors that must be overcome before a successful deployable water quality monitoring system can be developed.

Several tasks were implemented to identify and analyze those factors that determine the performance of off-the-shelf water quality sensors deployed in a realistic aquatic environment for up to 6 weeks and to improve sensor designs. These tasks included:

1. a literature survey of problems and solutions associated with biofouling of sensors to establish design modification to existing sensor packages,

2. testing of a method to eliminate biofouling,

3. long-term (6- to 8-weeks) testing of the probe packages in a realistic aquatic environment, and

4. comparison of long-term probe performance to simultaneous parameter measurements using laboratory standards

SECTION 2

CONCLUSIONS

Laboratory and field tests show that uncertainties in the performance of off-the-shelf water quality sensor packages preclude their use for unattended long-term field deployment. The following general conclusions about the sensors were drawn:

1. The Ocean Data sensor package is the most susceptible to physical damage. Extreme care must be taken in handling and in operations. The other sensor packages (Hydrolab and Martek) are essentially the same and cause some concern in calibration procedures.

2. For unattended, long-term deployment (greater than 10 days) reliability, stability, and maintainability of the sensors are unsatisfactory. The most significant problem is in circulator failure in the Dissolved Oxygen probe.

3. There is a considerable stabilizing period required for the sensor packages to adjust to environmental conditions. After a period of time, they appear to stabilize and remain stable until major difficulties occur, e.g., circulator failure.

4. New and reliable calibration programs must be designed and implemented for sensors used in long-term deployment. (Sensor manufacturers do not provide adequate calibration procedures.)

5. Biofouling in fresh water appears to be controllable.

6. Martek and Hydrolab temperature sensors perform reasonably well; the Ocean Data temperature sensor performs well for about 2 weeks and then begins to deteriorate.

7. The Hydrolab pH sensor is fairly stable, more so than the Martek or Ocean Data, but all three sensors show some tendency to be affected by time and/or fouling. The Martek seems to be affected by time alone since biofouling was effectively eliminated. Hydrolab and Ocean Data would probably perform better if kept free of biofouling. However, elimination of the drift characteristics, which are probably due to the inherent design of the circuits, would require design of a more stable system.

8. Conductivity measurements are very erratic. No definite conclusions could be drawn except that measurements of freshwater conductivities would be very unreliable due to the large uncertainties involved.

9. The Hydrolab and Ocean Data Dissolved Oxygen sensors perform well as far as linearity and stability are concerned. However, the large uncertainties involved would introduce an error of 20 percent or more.

These general conclusions are substantiated by more detailed analysis of each sensor system. The variables measured over the extended period are discussed below.

TEMPERATURE

Both Martek and Hydrolab temperature sensors give good performance over a 41-day period of exposure to a freshwater environment at a temperature range of 27 to 39°C.

The Ocean Data is stable for a 2-week period but tends to be sporadically erratic for the next 2-week period. After thirty days of exposure, the Ocean Data temperature sensor becomes very unreliable.

All three probes are readily calibrated for good linear tracking over the temperature range.

pH

The Hydrolab pH sensor is stable with respect to time and fouling.

The Martek pH sensor is stable at the lower end point but at the upper calibration point tends to drift as a function of time.

The Ocean Data pH sensor is fairly stable if kept clean, but is affected by fouling, especially at the lower calibration point.

The pH sensors for all three probes will track within ±0.5 pH units of the calibration curve existing at any particular time.

After a period of adjustment, the Hydrolab and Martek pH sensors remain stable for 12 days in fresh water. The Hydrolab pH sensor may be more sensitive to environmental degradation than the Martek, but no overall time dependence was observed for either unit.

CONDUCTIVITY

Conductivity is difficult to measure accurately in freshwater because the uncertainty in the observed values is often of the same order of magnitude as the range of values being measured.

At high conductivities, the uncertainty can be reduced to about 10 percent or less.

Due to the large uncertainties, it is difficult to calibrate the sensors accurately.

Assuming that the conductivity of the water to be tested does not change significantly with time, the average of the sensor readings over a period of time closely approximates the actual conductivity. However, if for some reason the conductivity were to change suddenly due to a sudden change in local water conditions (e.g., the passing of a wet weather front), the sensor would not be sensitive to the change unless the change were of the order of magnitude of several standard deviations. Even then it would require some time period after the change before the change could be statistically determined.

The standard deviation of the conductivity difference is of the order of 50 micromho/cm which will create a large relative error for any given Hydrolab measurement in water of low actual conductivity.

Tests in various environments, from fresh water to saline, will tend to eliminate some of the difficulty in assesssing the conductivity sensors.

DISSOLVED OXYGEN

The Hydrolab and Ocean Data Dissolved Oxygen sensors track linearly over a dissolved oxygen range of 0 to 20 and 0 to 17 mg/l respectively.

The indicated dissolved oxygen values will be within ±2.0 mg/l of the actual dissolved oxygen concentration.

The Martek Dissolved Oxygen sensor consistently deviates from the standard. This may be due to the calibration procedure, which is a 1-point calibration. The linearity of the sensor response cannot be guaranteed.

BIOFOULING AND "KILL ZONE"

A "kill zone" is an easily implemented mechanism for reducing biofouling by using a housing coated with an antifouling paint.

SECTION 3

RECOMMENDATIONS

Many physical and electrical problems were encountered in calibrating the sensors. The Ocean Data package, in particular, was very unwieldy and easy to damage. If the probes are to be deployed unattended for long periods of time the initial calibration should be refined. Suggested refinements are:

1. Multiple point calibrations. Present procedures require only one point for calibration. To ensure more accurate data collection, several calibration points should be used.

2. The calibration should not be a "one-time" calibration. Several readings of the sensor to be calibrated, taken over a period of several hours, should be averaged and the sensor set to the average value. The value of the parameter being measured should be constant.

A continuation program should include the following procedures:

1. Develop and test calibration techniques for each sensor under various environmental conditions.

2. Examine the feasibility of increasing the number of parameters that may be monitored.

3. Develop and evaluate new sensor designs to meet long-term deployment requirements.

4. Deploy and evaluate the performance of water-quality sensors under various field environments.

5. Under various field environmental conditions, evaluate individual sensors and/or sensor packages available from other manufacturers.

6. Continue a state-of-the-art review of sensor design technology, including a review of the latest work being done in environmental, medical, and space sciences.

7. Initiate a study into DO membrane structures, especially in the area of impregnated membranes using toxic, antifouling materials as the impregnating agent.

8. Develop a field testing laboratory, or mobile unit, to evaluate all sensors to be considered for long-term deployment.

In studies of the "kill zone" concept for controlling biofouling, the design of a more reliable, algae-resistant probe and probe housing should include the following characteristics:

1. Requirements for design of circulating system for remote water quality sensors

   a. low-current d.c. submersible pump

   b. d.c. power source, probably solar assisted

   c. non-corrosive structural material

   d. to reduce current drain, the power supply should have

      - low hydraulic resistance
      - complete change of water in minimum possible time

   e. flow regime should be turbulent to obtain good mixing and thorough flushing of "old" water sample

   f. the design of an optimum probe arrangement should be investigated to accomplish characteristics d and e

   g. resistance to biofouling or corrosion

   h. must not fail to operate for at least a 6-week period in various water environments

   i. must circulate water about the end of the dissolved oxygen sensor

2. Antifouling compounds

   a. scientific study of leach rates and their effect on sensor performance

   b. study of the different organo-metallic compounds

   c. determination of the optimum thickness of paint coatings and surface roughness

SECTION 4

BACKGROUND

Early attempts to remotely monitor river water quality resulted from increased demand for water due to population and industrial growth. Planners learned that limited water resources could be better managed with the more complete knowledge of river processes afforded by continuous monitoring. Thus, in the late 1950's the effort to develop remote river water quality monitoring systems was greatly accelerated in both the United States and Europe. Davies (1972) describes the European effort which attained many operational goals in the late 1960's. Typical of the European effort was work by Cooke and Woodward (1970) who developed a monitoring system for the River Trent. They measured temperature, dissolved oxygen, pH, and conductivity at numerous stations located to provide data on the pollution dispersion capabilities of the river. The problem of environmental degradation of the sensors was alleviated by weekly sensor cleaning and semimonthly calibration. Best (1974) reports similar objectives and results from research done in Scotland.

One early American effort was the ORSANCO project documented by Klein et al. (1968). ORSANCO, operated on the Ohio River, was begun in 1960 and consisted of 14 stations monitoring temperature, dissolved oxygen, pH, conductivity, redox potential, and solar radiation. Like its European counterparts, this research was designed to augment the management alternatives of regional planners so that new industries might be located in areas with the greatest potential for pollution dispersion. The problem of environmental degradation was bypassed because of the stations' easy accessibility for the frequent cleaning and maintenance of the sensors.

Palmer and Izatt (1970) reported the use of submersible recording water quality sensors during work for the Ontario Water Resources Commission. A one-quarter inch (6.35-millimeter) magnetic pipe was used to record water quality data in a project to investigate chemical and physical characteristics of a section of Lake Ontario, Canada. Problems of biofouling were alleviated through frequent sensor cleaning.

West and Floyd (1976) designed and operated a system for gathering baseline data on streams. Although the water quality parameters measured were not different from previous systems, the field instruments were powered by battery and solar sources. Previous inland systems had utilized power via transmission line; however, power requirements for field operators can now be met by existing technologies (LeBarge Inc., 1976, and Hydrolab Inc., 1975). Physical and biological influences impaired the performance of some sensors but weekly visits to cleaning and calibration provided for reliable results.

Smith (1973) designed a buoy system for monitoring temperature, dissolved oxygen, and conductivity in Narragansett Bay, Rhode Island. The data buoy was operated for over 100 days during which time severe problems of biofouling were encountered. Biofouling was caused primarily by Bryozoa and Hydroids, which are animals, not vegetation. Growth rate of these organisms increased as water temperature increased. The marine growth limited permeation of dissolved oxygen through the probe membrane causing inaccurate and unreliable readings. The electrolyte solution within the membrane became contaminated with suspended sediments, which might have affected probe performance. The duration of reliable dissolved oxygen readings was not explicity determined. Temperature thermistors and conductivity electrodes were covered by marine growth, but their performances were not impaired.

The U.S. Geological Survey, Baton Rouge, has devised a means of eliminating biofouling and physical damage to sensors at two continuous recording water quality stations in Louisiana (R. Lewis, personal communication, 1978). A submersible pump lifts water into a 5-gallon (19-liter) sump through which it continuously flows. Water quality sensors are submerged in a sump located in a small field station. Water quality readings are periodically made after a timer activates the sensors. After the readings are determined, a second timer activates another pump that discharges a hyper-chloride solution into the container. The resulting acidity kills any organisms that might have attached to the sensors. Within minutes the flushing action of the submersible pump replaces the acidic solution with river water, thus restoring the desired water medium before the next sensor observations.

The literature on remote water quality monitoring reveals that most stations are remote mainly in the sense that technicians are not manually recording data. Most stations are accessible to power via transmission line and are easily accessible by car or truck. All stations recorded data on strip charts, paper or magnetic tape, or via local telemetering devices.

Of the environments in which monitoring systems have been tested, Narragansett Bay (Smith, 1973) is most similar to conditions in the Louisiana wetlands: experimental sites are not accessible by land or power lines, and rapid biofouling is likely to occur in the estuarine environment. However, Smith did not test the duration of reliable sensor performance.

In previous work conducted at LSU (Gasperecz, 1978) the difference between Hydrolab and auxiliary dissolved oxygen data was of primary interest, because of the general agreement among current researchers that the longevity of the dissolved oxygen probe is the limiting factor affecting the duration of reliable oxygen or sensor performance (Lewis, U.S. Geological Survey; Smith, Louisiana State University; and West and Floyd, U.S. Army Engineer Waterways Experimental Station, personal communications).

The importance of proper water circulation around the dissolved oxygen probe was clearly illustrated in the data obtained in the LSU experiments. A sharp change was noted in the difference between Hydrolab measurements and

auxiliary measurements corresponding to the point at which the circulator ceased functioning. The circulator failure was probably caused by a combination of power drain and physical resistance due to sediments and organic detritus in the area of the pin on which the circulator rotates. Negative difference values indicated lower dissolved oxygen measurements for the Hydrolab than the auxiliary sensor (due to oxygen depletion at the Hydrolab probe membrane). It is clearly evident that water circulation is essential for reliable dissolved oxygen measurement and that circulator failure limits the longevity of accurate sensor performance.

The LSU data relating to performance of the dissolved oxygen subsystem form a base against which future comparisons of probe performance can be made.

It is noteworthy that the data presented by Gasperecz were obtained in mid to late summer. This is significant because the growth rate of aquatic organisms is highest during this period due to increased insolation and water temperature. The estimates of duration of accuracy presented are based on data derived during the period when the rate of biofouling would be at its peak and are probably shorter than those that would be derived during periods of cooler weather.

The major technical problems encountered in establishing a remote, long-term water quality monitoring system are biological fouling of the sensors and stability of this sensor with respect to its calibration. Chemical fouling (corrosion) and physical fouling (deposition of mud, sand, debris, etc., on the sensors and sensor housing) are present but do not pose as serious a problem as biological fouling. The main problem of physical fouling is interference with the dissolved oxygen probe circulator. Early failure of the circulator is usually due to excessive physical degradation.

The primary problem of biological fouling is the growth of aquatic organisms on the active surfaces of the sensors. Fouling of non-active surfaces presents a nuisance but does not interfere with parameter measurement. Several surveys and laboratory tests were initiated to determine possible methods to alleviate or eliminate biofouling of the probe surfaces. Possible solutions were considered in LSU laboratory projects and are summarized below.

1. <u>In situ ultrasonic cleaning of probes</u>

A feasibility study of this method indicates that ultrasonic cleaning could be successfully employed. Such a system has been used by Lewis of the USGS, Water Resources Division, Baton Rouge, Louisiana. However, Mr. Lewis had the advantage of direct a.c. line voltage as the power source, unlike the situation of a remote sensor utilizing a d.c. power supply. One of the major disadvantages of ultrasonic cleaning is the relatively large amounts of power required compared to the power requirements of the sensor package itself. In addition, the need to convert the low voltage d.c. source into a high amplitude a.c. supply, the potential damage to the dissolved oxygen probe membrane, and the additional mechanical complexity due to the addition of

the ultrasonic transducer, make the use of ultrasonics less attractive. A laboratory test at LSU resulted in giving low priority to this mechanism for probe cleaning.

2. In situ generation of sodium hypochlorite from sea water

This method has been used successfully in industrial applications by Connolly (1973) and Lamb (1972). The passage of sea water through an electrochemical cell generates sodium hypochlorite and hydrogen gas. Such a cell could be used inside a closed container to generate a toxic level of hypochlorite. Although this method would probably work well to prevent biofouling, there are several disadvantages: the method will work only in sea water and would not be applicable to fresh water monitoring, the hydrogen gas generated as a byproduct would have to be removed, the resultant chemical products may interfere with the probe readings, and a circulating system would be necessary to periodically bring a new water sample into the container. These considerations make in situ generation of sodium hypochlorite a feasible but unattractive solution.

3. Local application of heat

It has been demonstrated in industrial applications by Anderson and Richards (1966) that an increase of approximately 50°F above ambient temperature for 30 minutes per week will prevent growth of mussels and barnacles, although this may not be true for algae growth, the predominant form of probe biofouling. Since most algae are active within a relatively narrow temperature range, a temperature increase of 50°F would probably increase the local temperature above the maximum tolerable temperature for most algae. It is not known how often the heat should be applied or how long each application should be in order to prevent algae growth. Potential drawbacks to this method are excessive power requirements, if frequent heat applications are necessary, and potential damage to probes.

4. Light-proof environment to suppress photosynthesis

Since algae are plants, they require light to grow and reproduce. Enclosing the probes in a light-proof enclosure should, therefore, be effective in suppressing algae growth. This would require a circulation system to periodically expose the probes to the water sample to be tested. The disadvantages of this method are that a circulation system would be needed, and that periodic flushing of the enclosure would expose the probes to fresh algae and thus reduce the effectiveness.

5. Local "kill zone" produced by toxic antifouling paints

Antifouling paints, in particular those based on organometallic tin compounds, have been found effective in eliminating biofouling in investigations by Caprari and Rascio (1972), Saroyan (1968), and Rohling et al. (1975). Since the probe surfaces cannot be directly coated with an antifouling paint without interfering with probe performance, it is proposed to generate a "kill zone" at the probe surface by enclosing the probes in a container that has been painted on the inside surface with a toxic paint.

There should be no interference with probe readings as the container would be flushed before each reading to bring in fresh water. The leach rate of the tin into water is slow enough so that the measurements would be completed before a high level of tin could accumulate. The leach rate would have to be fast enough, however, so that a toxic level could be attained before the next measurement is made. Since a faster leach rate reduces the effective fouling resistant lifetime, it may be necessary to develop a paint formulation that provides both the desired effective lifetime and sufficiently high leach rate.

The disadvantage of this method is that a circulation system would be required, thereby increasing the complexity of the total system.

6. Periodic injection of biocide

The use of a general purpose biocide such as sodium hypochlorite has been used successfully in industrial applications by Connolly (1973), Lamb (1972), and Anderson and Richards (1966). A biocide should also be effective in eliminating biofouling of the probe package. If the probes are enclosed in a container into which the biocide is periodically injected, a sufficient concentration will produce a toxic level. This procedure has the disadvantages of requiring a circulating system for the water and a biocide injection system. Also, the long-term effects of the biocide on probe operation would have to be investigated.

7. Incorporation of toxic compounds into dissolved oxygen membrane

The parameter most sensitive to biofouling is the dissolved oxygen probe because of algae growth on the membrane surface which interferes with the migration of the oxygen molecules across the membrane. The U.S. Navy has developed structural plastics that have a toxic compound incorporated directly into the structural matrix, thereby making the material highly resistant to biofouling. These studies were reported by Eller et al. (1970) and Dyckman et al. (1974). A similar procedure should be applied to the dissolved oxygen membrane to render it resistant to biofouling.

Of the seven possible methods of reducing biofouling discussed above, the use of antifouling paints to generate a local "kill zone" is the most feasible because it is the simplest to implement, requires a minimal increase in power requirements, and has been proved effective. In addition, the container used to generate the "kill zone" will also serve as a deterrent to physical fouling and protect the probes from excessive wave action.

Antifouling paints have been available for many years, but their performance has been questionable (Smith, 1973). The U. S. Navy has developed coatings of optical quality (transparent) to inhibit growth of aquatic organisms on submarine periscopes (Montemarano and Dyckman, 1972). These organometallic polymers (OMP) have been tested for up to 5 months with complete antifouling performance. Use of an OMP to coat the sensor's non-probe components will substantially reduce overall plant and animal growth.

More recently, the U. S. Navy has developed antifouling composite materials designed for utilization in construction of buoys, seawater piping, shore structures, etc. (Montemarano and Cohen, 1976). These organometallic-based composite materials have demonstrated complete antifouling performance for up to 34 months. Utilization of one of these composite materials for the construction of the structural components of a water quality sensor would effectively eliminate biofouling on all non-probe surfaces.

The use of antifouling coatings and composite materials could solve the biofouling problem on all parts of a water quality sensor with the exception of the water quality probes. The probes' sensing components (dissolved oxygen membrane and cell, conductivity electrodes and thermistors, temperature thermistor tube), as they presently function, cannot be coated with or constructed of antifouling materials and still maintain operation. A means of preventing organism attachment to the probes must be developed to safeguard water quality sensors completely from biological degradation.

Finally, a workshop sponsored by the U.S. Environmental Protection Agency in Las Vegas, Nevada (Wruble, Koutsandreas and Pijonowski, 1978), substantiated the need for new research and development efforts in the area of deployable sensor development.

SECTION 5

INSTRUMENTATION, EQUIPMENT, AND FIELD PROCEDURES

PROBE PACKAGES

Four complete probe packages were obtained for use in this research: a Hydrolab Surveyor Model 6D, two Martek IV's and an Ocean Data Model 101A. Each of the packages is capable of measuring temperature, conductivity, pH and dissolved oxygen. The Hydrolab is the property of Louisiana State University, the two Martek's were obtained on loan from the U.S. Environmental Protection Agency, Las Vegas, Nevada, and the Ocean Data Display unit was borrowed from the Ocean Data Corporation for 4 months.

However, because of equipment need of maintenance and repair, an initial 12-day test using only the Hydrolab and one Martek probe was conducted. Also, before long-term testing could begin, one of the Martek probes developed problems in the pH and dissolved oxygen circuits. Thus, the long-term test utilized only three probe packages.

LABORATORY STANDARDS

The measured parameters were compared to standard values as measured by the following methods:

Conductivity--The conductivity of the water in the proximity of the probes was measured by a HACH portable conductivity meter, Model 163000. The calibration of the portable meter was checked periodically.

pH--The pH of the water in the proximity of the probes was measured by a Scientific Glass Instruments, Inc., digital mini pH meter. The meter was calibrated prior to each measurement of pH.

Temperature--The temperature of the water in the proximity of the probes was measured with a laboratory grade mercury thermometer.

Dissolved oxygen--Dissolved oxygen in the proximity of the probes was measured by a Winkler test on water samples taken before and after the sensor readings were recorded.

The Winkler test was performed according to the procedure described in "Standard Method for the Examination of Water and Wastewater," (APHA 1976).

AQUATIC ENVIRONMENT

To simulate actual field conditions as closely as possible, yet still have a convenient, easily accessible test site, the comparative tests were run in a university fresh-water research pond operated by the LSU Department of Agriculture. The pond is located in a university research area that provides protection from vandalism. The pond is roughly 900 feet (275 meters) long by 200 feet (61 meters) wide and has a maximum depth of approximately 5 feet (1.5 meters). The pond is sufficiently rich in algae and other aquatic organisms to provide a realistic sensor environment.

MOUNTING PLATFORM

The sensor packages were mounted in a physically stable configuration that also provided for easy access for data readings and any required maintenance. For this purpose, a platform was constructed and erected in the research pond.

The readout consoles and power supplies were placed on the platform shelves (Figure 1) and the sensor packages were suspended so that the top of the sensor housings were just below the water surface. Before data were taken, the sensors were raised so that the active probe surfaces were just below the water surface.

POWER SUPPLIES

Power supplies for the Martek probe sensors were supplied by two 12-volt automobile batteries. The Hydrolab systems used nickel-cadmium batteries for the sensors and a separate 6-volt battery for the dissolved oxygen circulator.

CONTAINER AND CIRCULATING SYSTEM

One of the Martek sensor pacakages was modified to test the proposed "kill zone" method of reducing biological fouling. A container was constructed of sheet aluminum to fit over the Martek IV sensor housing (Unit Number 2). The container is cylindrical with a funnel shaped exit plenum to which is attached a submersible 12 volt d.c. pump. The top of the cylindrical container has a one-half inch (12.7 millimeter) gap to allow water to enter. The inlet is covered with fiberglass mesh to prevent debris and large aquatic life, which could damage the pump impeller, from entering the container. Figures 2 and 3 show the container system.

The interior of the container is painted with two coats of Sears Antifouling Bottom Paint with tributyltin fluoride as the active toxic agent.

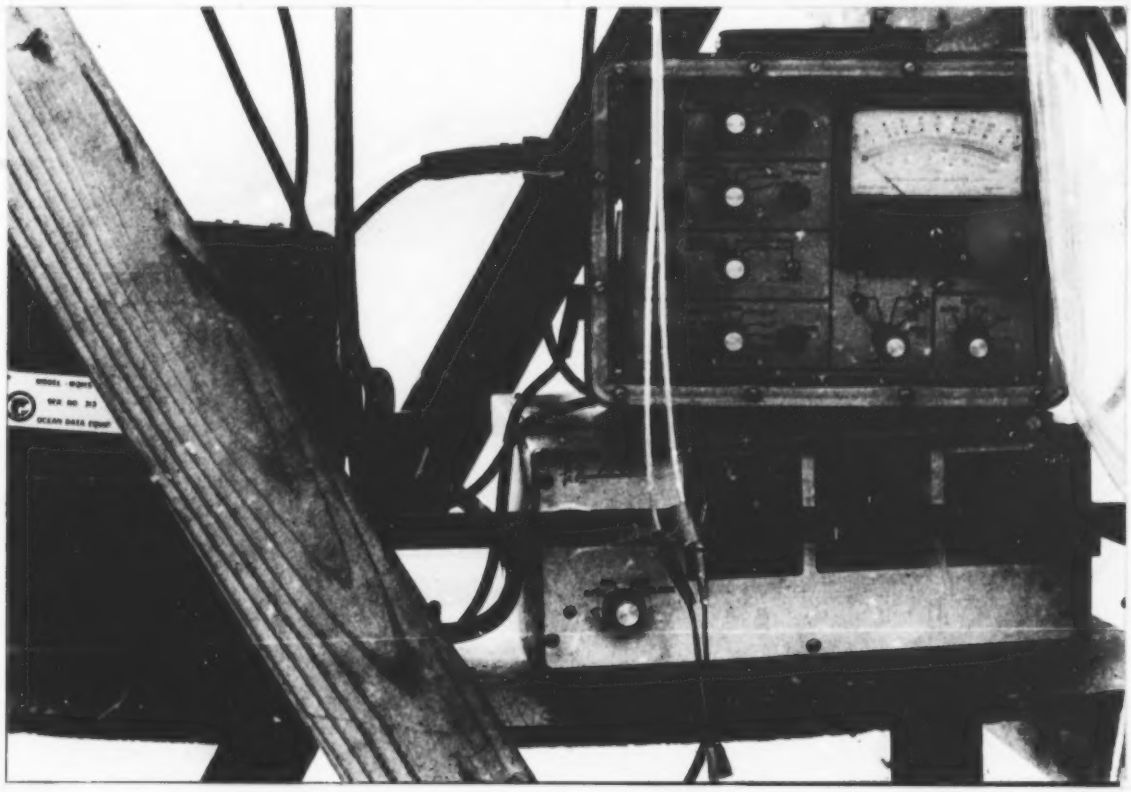

Figure 1. Instrumentation read out devices.

An automatic timer is used to activate the pump for 2 minutes every 4 hours in order to bring a new water sample into the chamber.

FIELD PROCEDURES

The following format was followed in acquiring all data points.

1. Apply power to sensor packages and the Hydrolab dissolved oxygen circulator. (Since the power supplies are depletable batteries, energy is conserved by turning on the sensors only when data are recorded.)

2. Raise sensor housings so that probes are just below water level.

3. Check that all circulators are operating.

4. Allow probe readings to stabilize (approximately 10 minutes), to alleviate the problems associated with warm-up periods.

Figure 2. Enclosure designed for Martek Probe.

The inside surface of this cone-shaped housing was coated with two coats of an antifouling paint (tributyltin flouride) to create a "kill zone" for combating biofouling of the sensors. The housing also contains a small pump to provide periodic flushing of the enclosure.

Figure 3. Side view of enclosure for Martek Probe.

5. Check pH and conductivity meters while sensors are stabilizing.

6. Take a water sample at the water surface between the probes, and immediately fix the dissolved oxygen content according to the procedures for the Winkler method as described in APHA (1976). Use "Alum Flocculation Modification" if required.

7. Record Hydrolab readings for temperature, pH, conductivity and dissolved oxygen.

8. Record values of temperature, pH and conductivity as measured by the other instrumentation.

9. Manually operate circulatory pump for 2 minutes. With pump off, record Martek IV readings for temperature, pH, conductivity and dissolved oxygen.

10. Record Ocean Data readings for temperature, pH, conductivity and dissolved oxygen.

11. Take a second water sample at the water surface between the probes and fix the oxygen content as before.

12. Check all probe readings to ensure that readings are stabilized.

13. Turn off all power supplies.

14. Lower sensor housings to original positions.

15. Check to ensure that everything is firmly in place.

16. Deliver water samples to the laboratory for immediate Winkler analysis and record the results.

Record data three times daily at intervals of approximately 4 hours (early morning, afternoon and evenings).

SECTION 6

RESULTS AND DISCUSSION

The data presented in this section were obtained from three sources: a 12-day test performed on the Hydrolab in three different water environments (Gasperecz, 1978) (Data Set I), the 12-day initial test of the Hydrolab and one of the Martek probes in a freshwater site (Data Set II), and the long-term (6-week) test of the Hydrolab, Martek and Ocean Data sensors in a freshwater site (Data Set III), the latter two testing periods being conducted in this current project.

Before being calibrated and deployed, the Hydrolab and Martek sensors were cleaned to ensure that no residual algae or sediment were on the active probe surfaces. The Ocean Data required no cleaning.

After removal from the water after a 6-week period, the probes were as shown in Figures 4 through 9. The Hydrolab and Ocean Data were significantly

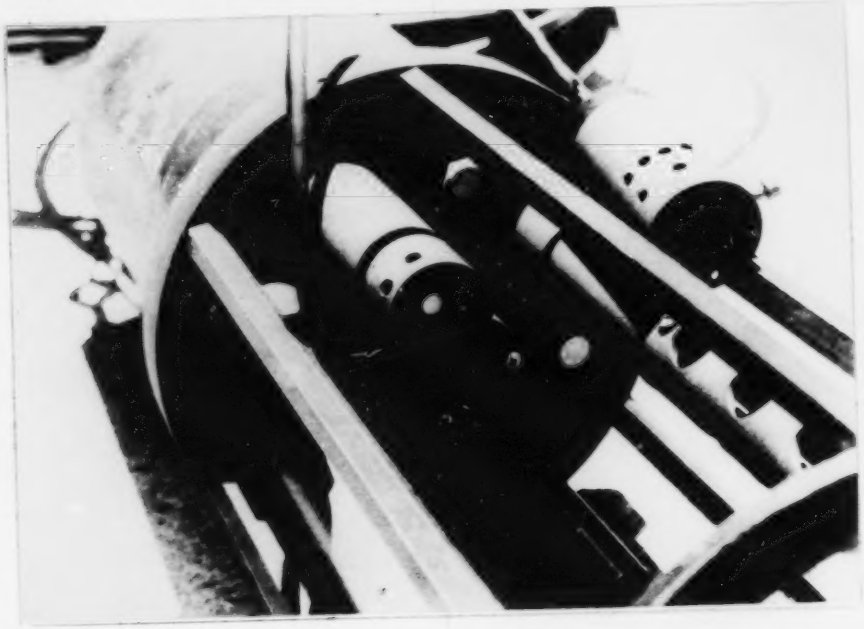

Figure 4. Martek Probe after tests.

This probe was protected over the 6-week period by the housing shown in Figures 2 and 3. Note the absence of biological growth on the sensor area.

Figure 5. Martek Probe and enclosure after tests.

This shows the biological growth attached to the housing protecting the Martek Probes (Figures 4 and 6) after 6-weeks of testing in a freshwater environment.

Figure 6. Martek Probe after tests.

Another view of the protected Martek Probe after the test period.

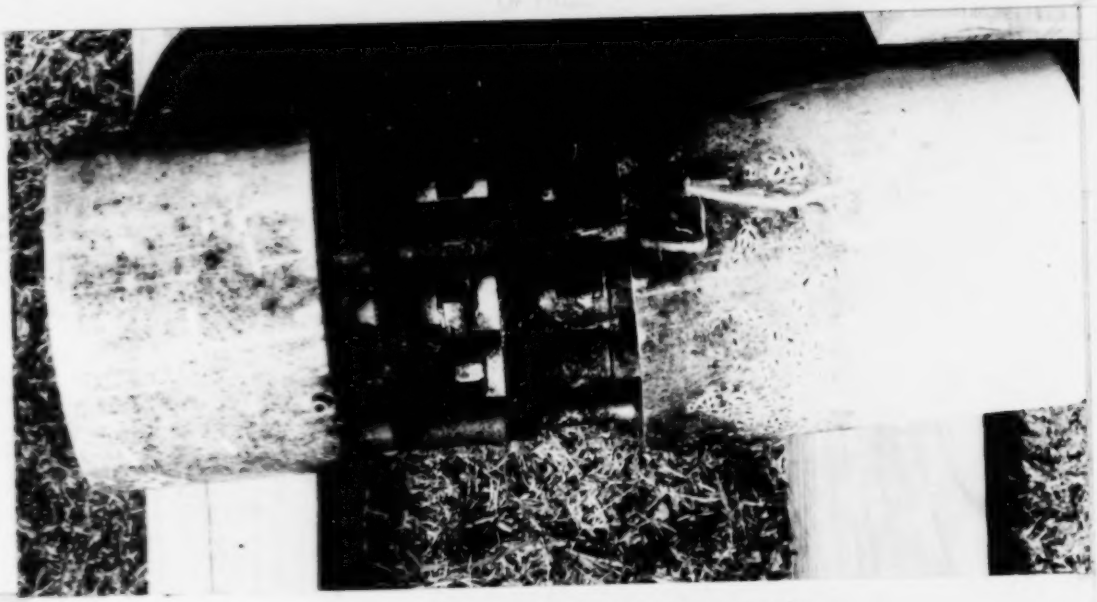

Figure 7. Hydrolab Probe after tests.

The biofouling which occurred over the 6-week period is shown. Note the linear markings to the right of the probe cavity, they are clean areas created by handling.

Figure 8. Ocean Data Probe after tests.

Considerable biofouling is evident on this housing and probe system as noted in the different gray scales on the photograph.

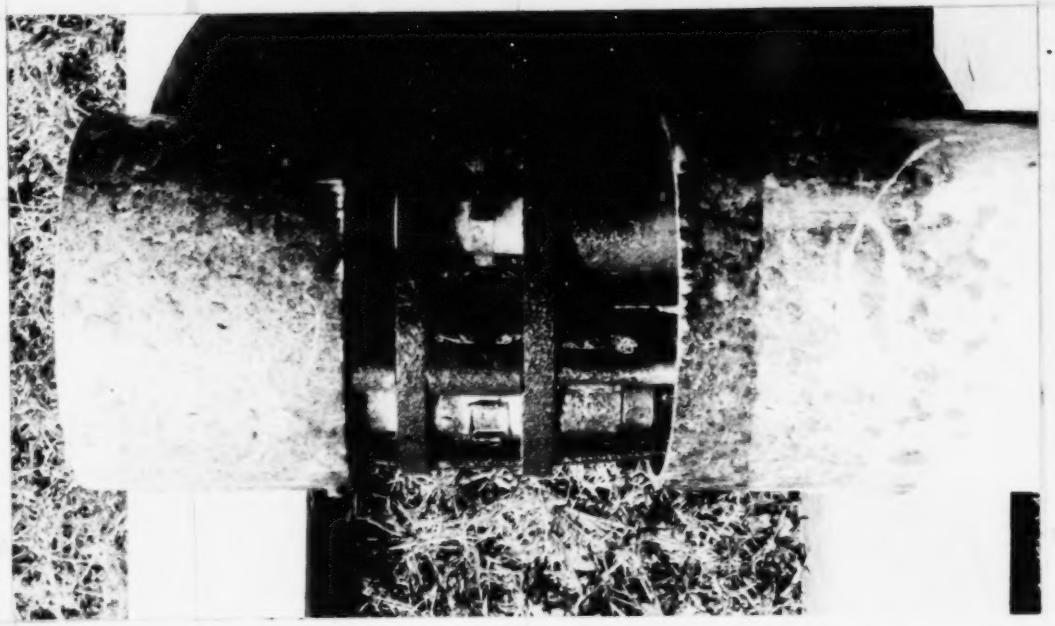

Figure 9. Hydrolab Probe after tests.

Another view of the biofouling which occurred during the 6-week test period.

covered with algae growth and other aquatic organisms. The Martek, which had been enclosed in the protective enclosure, showed no significant difference from its initial condition except at the upper end of the housing which was not completely protected by the antifouling paint. It is evident that the antifouling paint is very effective in eliminating biofouling. It is also possible that the agitating action of the circulating water (2 minutes every 4 hours) contributed to the reduction in biofouling. Additional support for this hypothesis is obtained from the observation of the Hydrolab sensors after removal from the water.

Examination revealed that the surface of the Hydrolab dissolved oxygen probe directly above the circulator was very clean and free of algae. In addition, the glass electrode of the pH probe was entirely covered with algae where exposed to the water, except for a small spot (0.5 cm x 0.5 cm) on the side facing the center of the probe package where the circulator impeller is located. Relatively clean areas on all the probes were observed at those locations where the probe surfaces were enclosed by a plastic support housing through which the sensors were mounted. The dissolved oxygen membrane was covered with a thin film of foreign matter which easily wiped off. The membrane was still transparent but had a cloudy appearance.

The Ocean Data pH, conductivity and temperature sensors were all completely covered by algae and other foreign material. The circulator, instead of a circular impeller as in the Hydrolab, consists of a vibrating

wedge positioned about one-sixteenth inch (1.59 millimeters) from the dissolved oxygen membrane. The dissolved oxygen sensor is positioned away from the other sensors and attached to the outer housing of the package, and the effects of the vibrator would not be felt by the other probes. The dissolved oxygen membrane was covered with a thin film of foreign material similar to the Hydrolab.

In the following discussion, the performance of each parameter is discussed separately.

TEMPERATURE

Of all the parameters measured, the temperature was the most stable. The results for Data Sets I, II and III are presented in Table 1 and plots for Data Set III are given in Figures 10 through 15.

The slopes of Least Squares Fit (LSF) ranged from 0.90 to 1.065 for all data.*

Coefficients of Determination, R^2, were greater than 0.93 in all but two cases.

The slopes of the curves (Figures 10, 12, and 14) are not statistically different from 1.0 at a 5 percent probability level except for two cases.

The 95 percent Confidence Intervals (CI) of the slope ranged from ±0.5°C to ±1.5°C. Seven of nine data sets had 95 percent Confidence Intervals between ±0.5 and ±1.0°C.

The Ocean Data temperature sensor performed very well for 15 days after which time the sensor began to give excessively large deviations from the standard temperature. This occurred twice for periods of about 3 days each, separated by a period of about 7 days of normal operation. After 30 days, the Ocean Data began to give increasingly high readings. This trend was continuing as the test ended.

The Martek was removed after 15 days of exposure to check the dissolved oxygen sensor. It was replaced after 1 day had elapsed. The temperature sensor was not adjusted, but the apparent slopes of the temperature curves changed from 0.955 to 0.902.

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* In the discussion of other parameters, the abbreviations LSF, R^2, and CI will be used.

TABLE 1. LEAST SQUARES REGRESSION OF OBSERVED TEMPERATURE AGAINST A DEFINED STANDARD TEMPERATURE

Data Source	Range of Temperature (°C)	Summary of Least Squares Fit (LSF)				
		Slope	Intercept	R^{2*}	0.95 CI†	NDP**
I, HL freshwater	29-33	0.934	2.293	0.79	±1.0	69
I, HL brackish	29-34	0.991	1.276	0.62	±1.5	78
I, HL seawater	25-32	1.065	-1.184	0.97	±0.7	62
II, HL freshwater	25-32	0.995	-0.728	0.93	±1.1	36
II, MK freshwater	25-32	1.013	-0.638	0.98	±0.6	29
III, HL freshwater	27-39	1.017	-1.300	0.97	±1.0	93
III, MK1‡ freshwater	27-39	0.955	0.732	0.97	±0.5	42
III, MK2‡ freshwater	27-39	0.902	1.930	0.98	±0.9	48
III, OD§ freshwater	27-39	0.986	-0.191	0.96	±0.7	41

* Coefficient of Determination, R^2

**Number of data points.

† Confidence Interval of the Slope

‡ The Martek probe was removed 1 day after 14 days exposure for a check of the dissolved oxygen sensor. The MK1 data are for the first 14 days exposure, and the MK2 data are for the 26 days exposure after the probe was redeployed. The temperature sensor was not adjusted.

§ After 14.7 days exposure, the Ocean Data temperature began to indicate excessive deviation from the standard temperature. The data given here are only for the first 14.7 days.

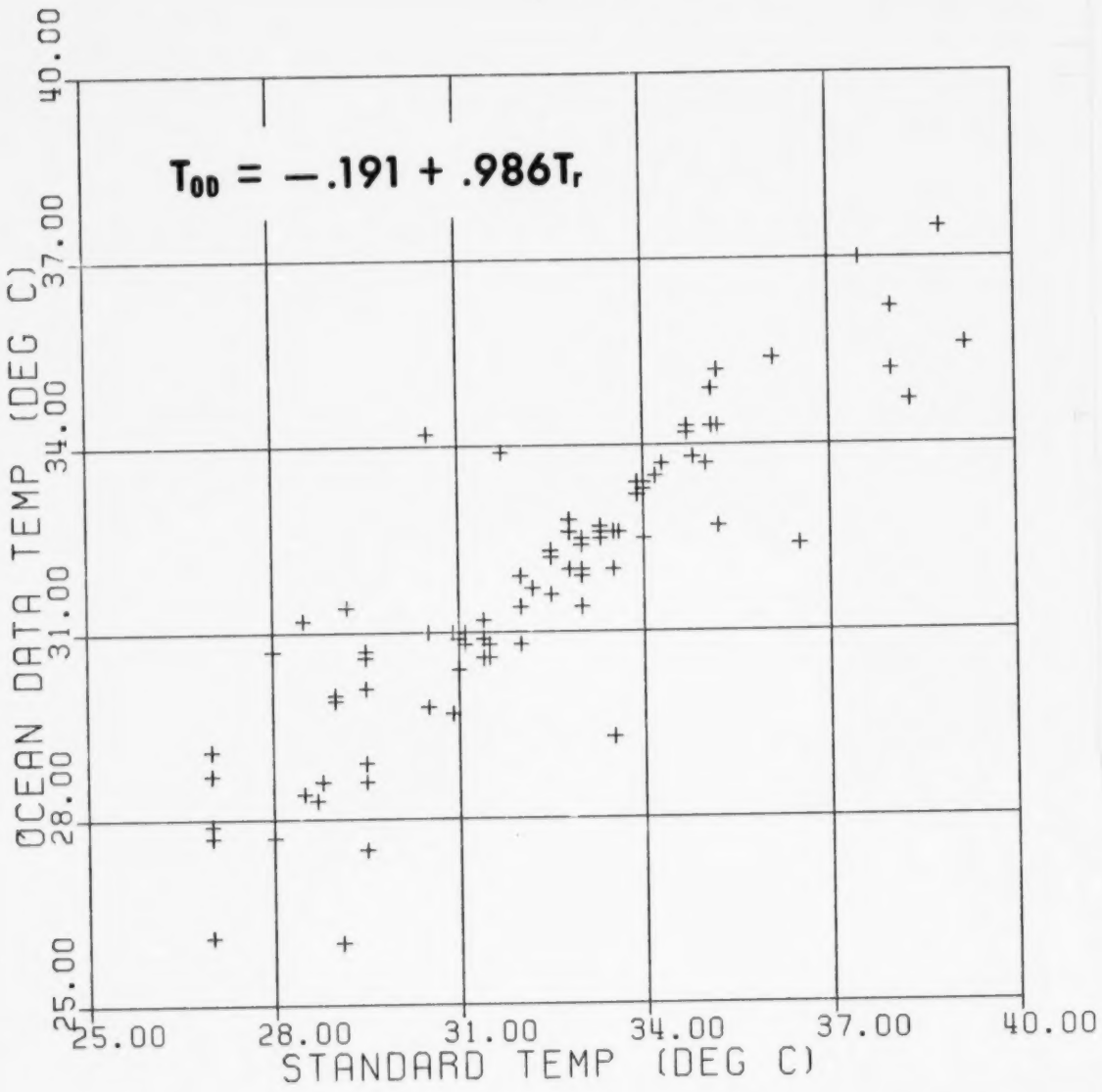

Figure 10. Ocean Data temperature vs. standard temperature, for Data Set III.

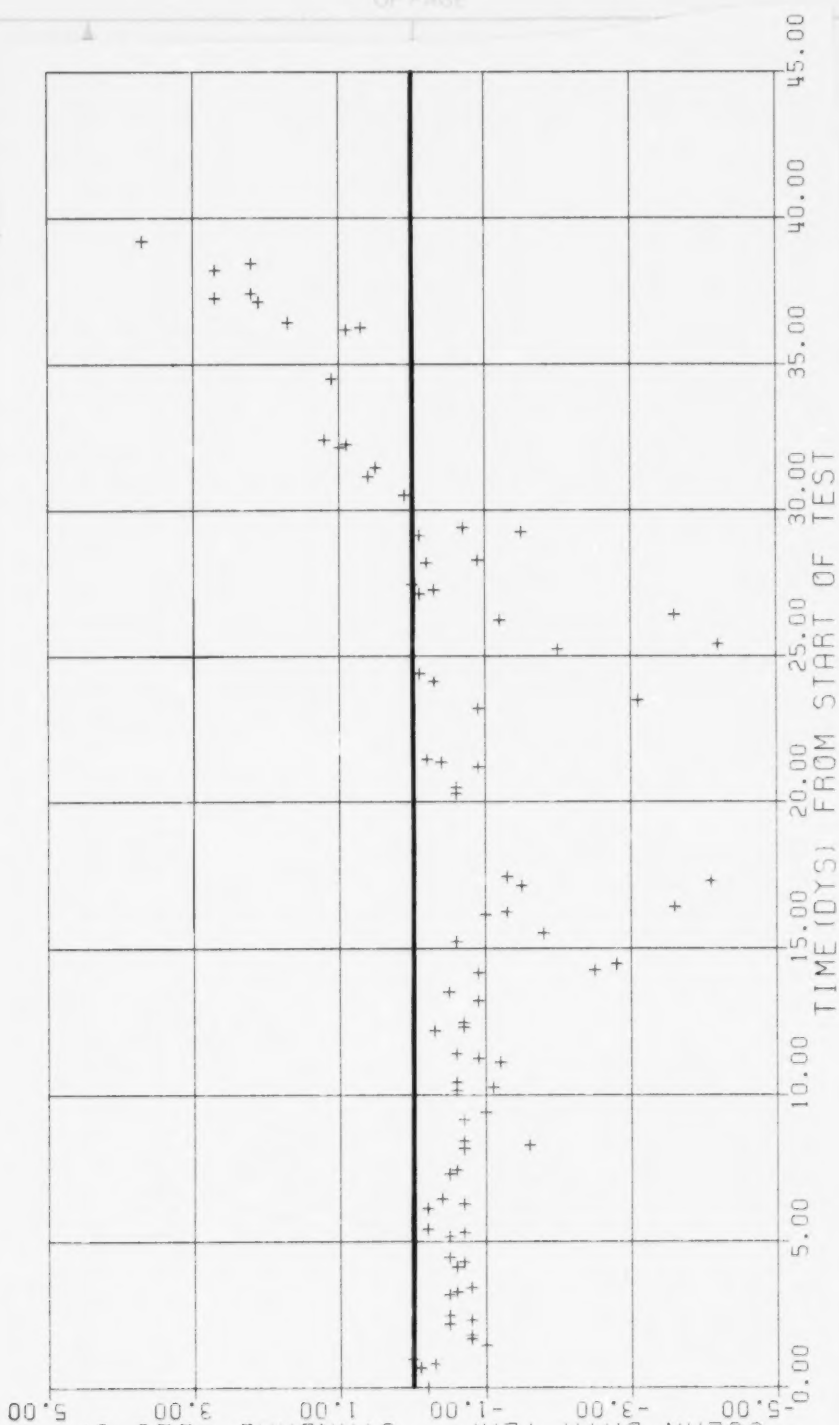

Figure 11. Ocean Data temperature vs. time, Data Set III.

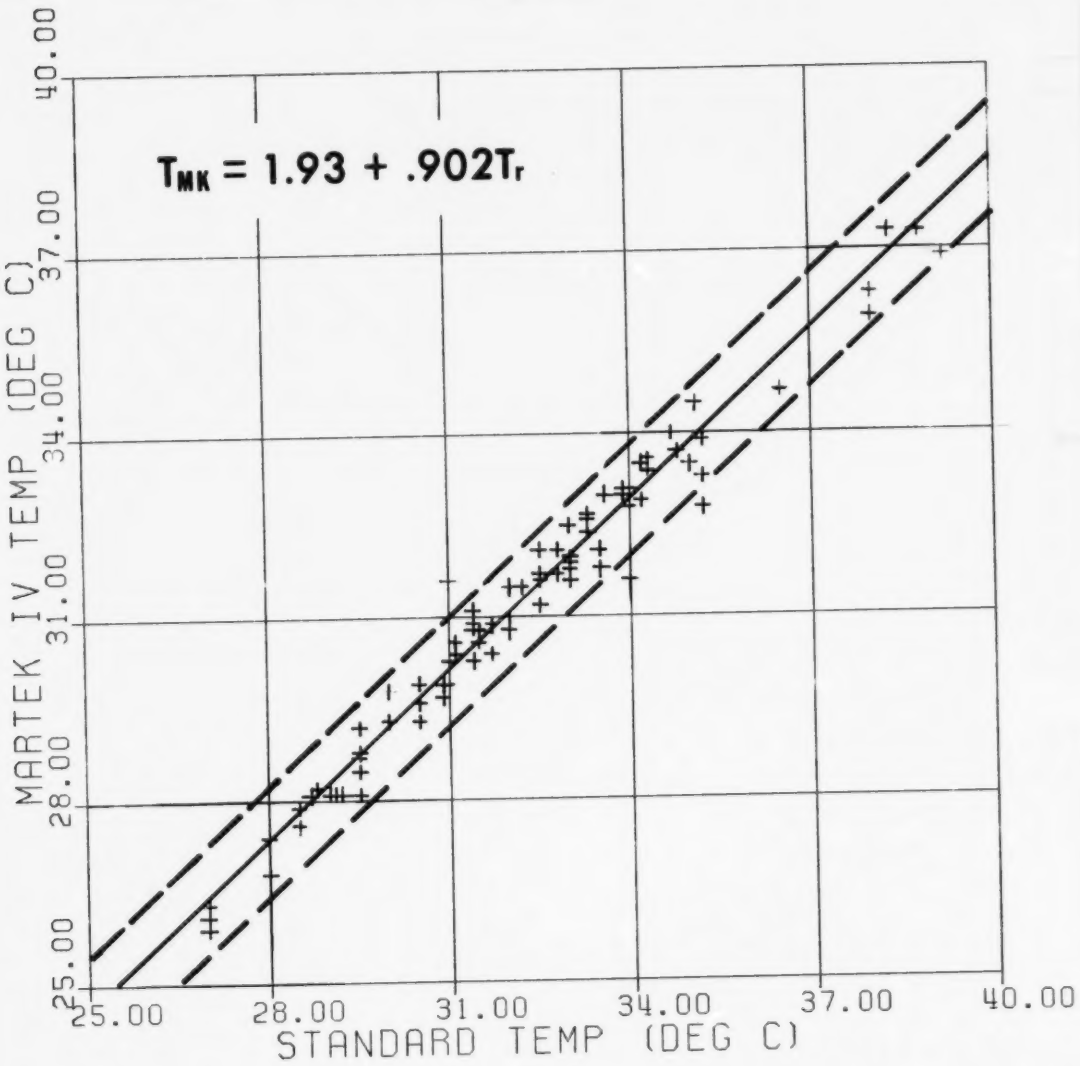

Figure 12. Martek IV temperature vs. standard temperature, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean temperature values for the Martek IV.)

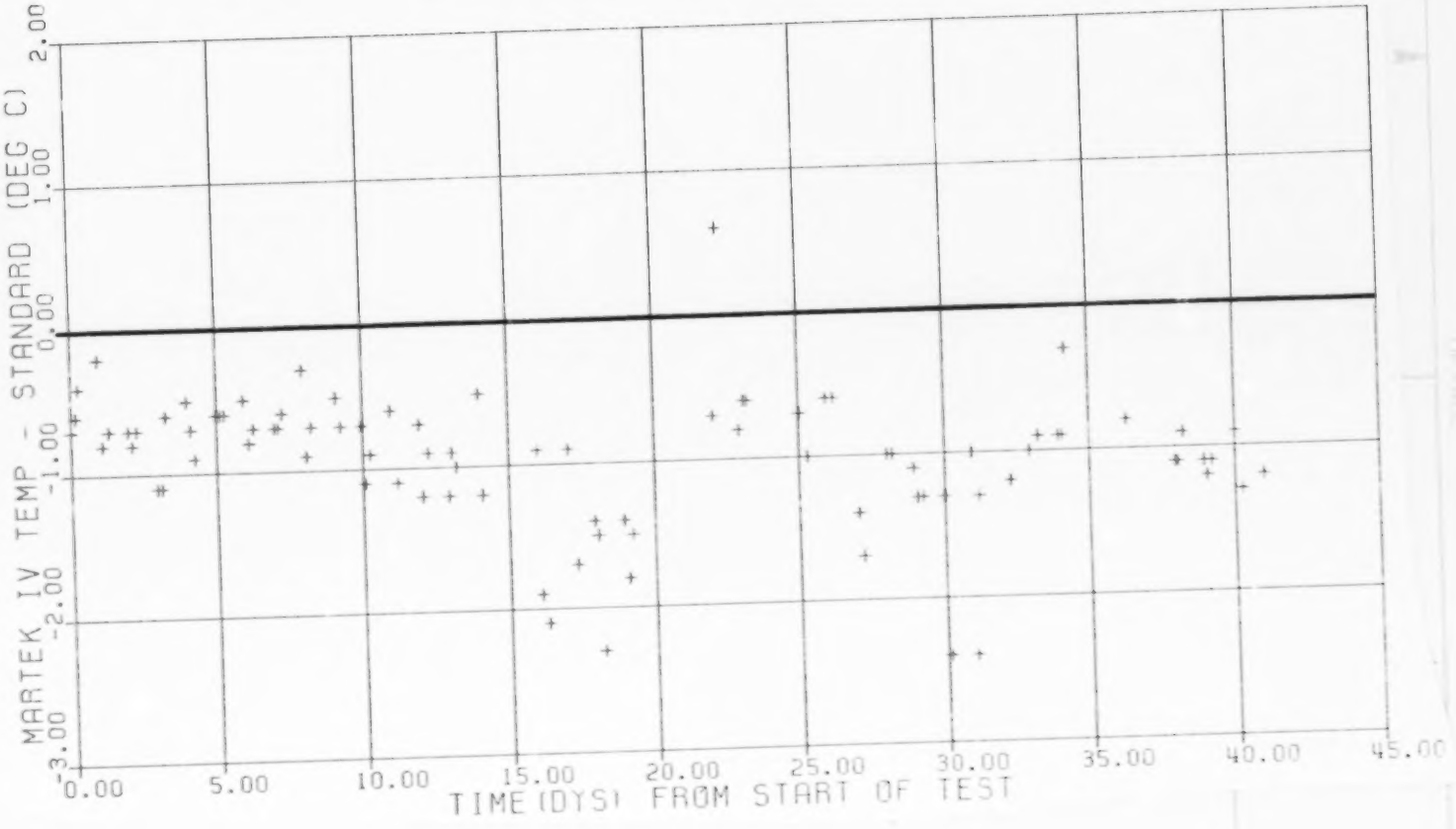

Figure 13. Martek IV temperature vs. time, Data Set III.

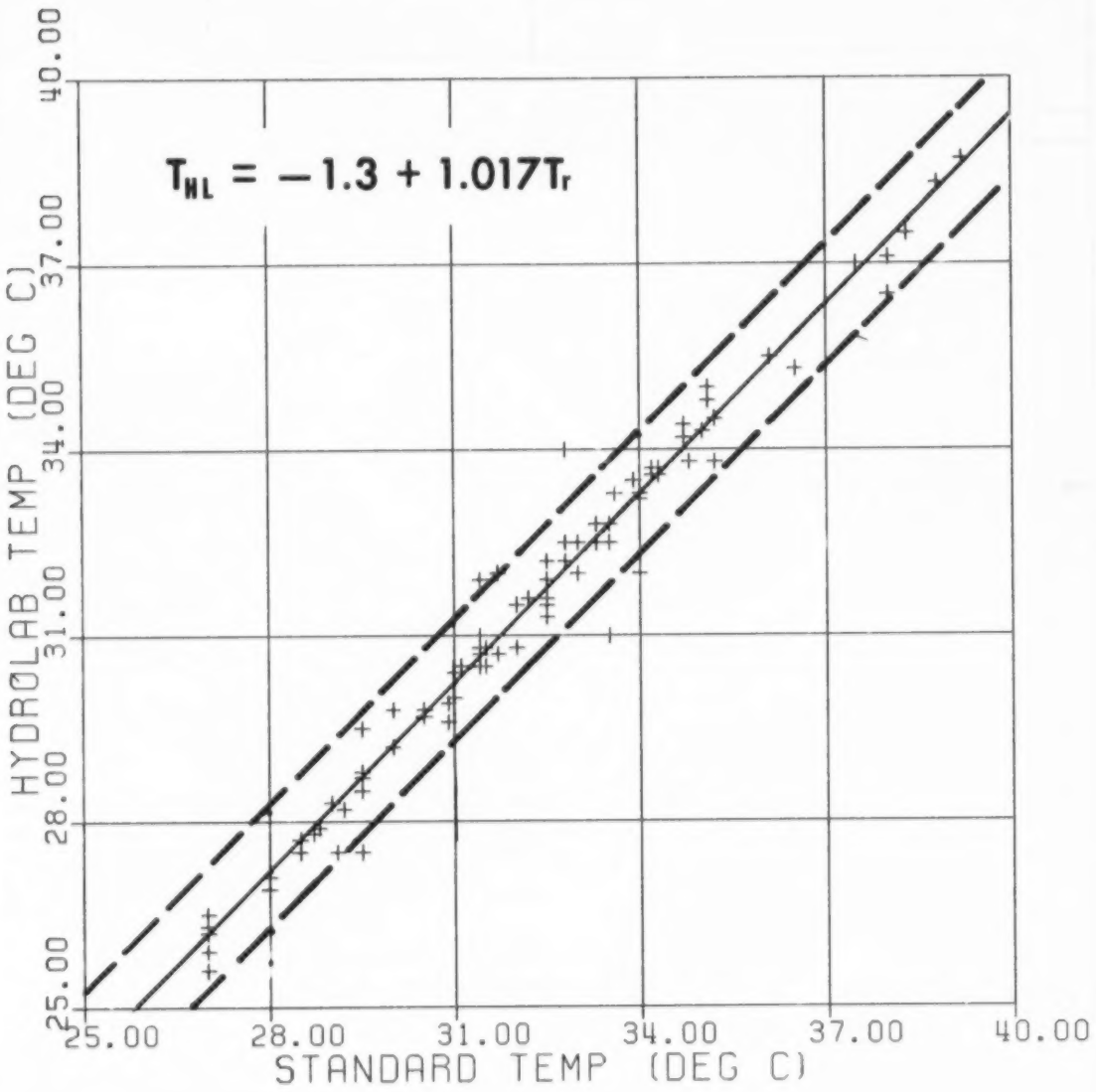

Figure 14. Hydrolab temperature vs. standard temperature, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean temperature values for the Hydrolab.)

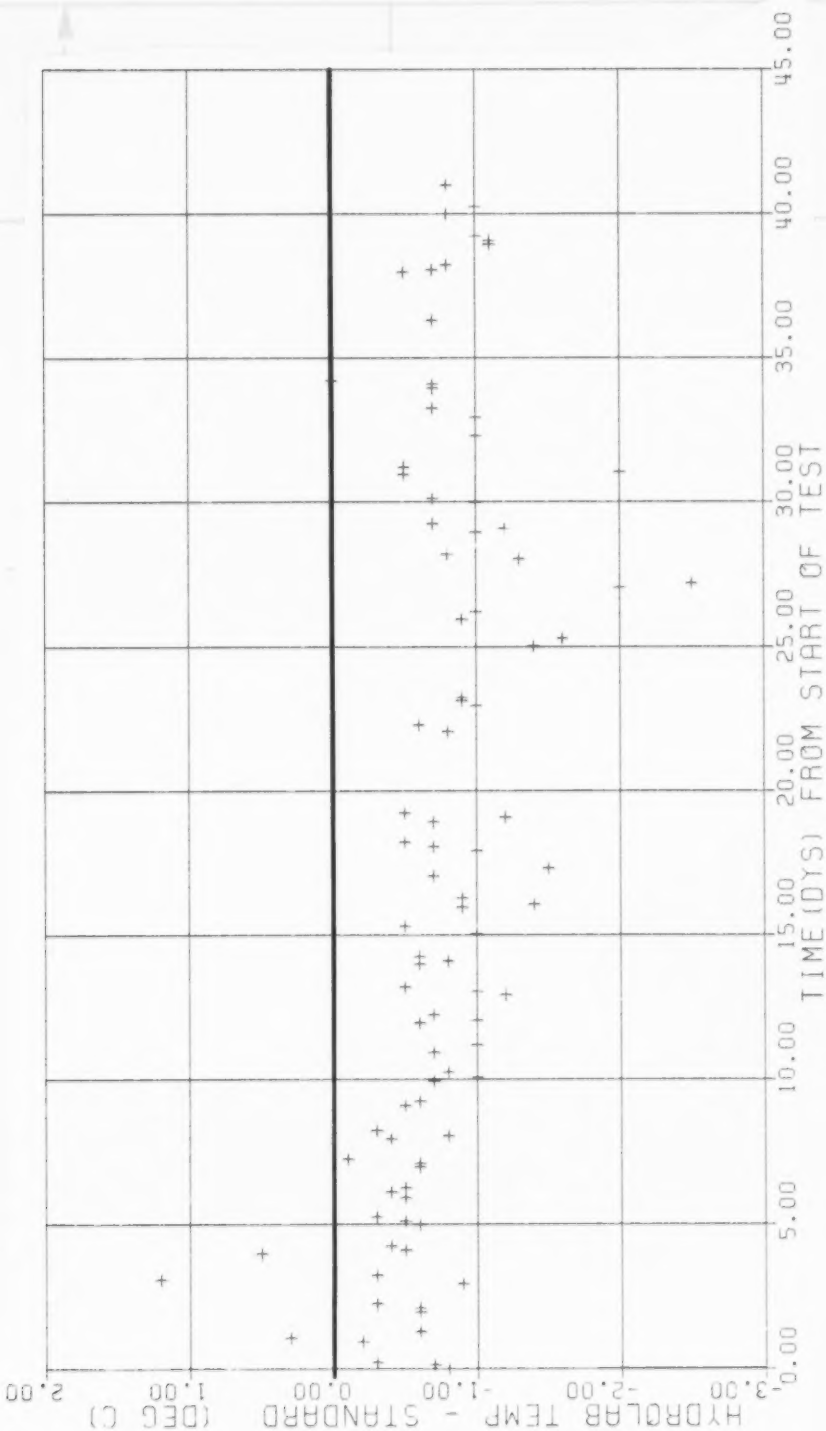

Figure 15. Hydrolab temperature vs. time, Data Set III.

pH

pH sensor analysis is presented in Table 2 for Data Sets II and III and plots for Data Set III are given in Figure 16 through 21. The following observations are noted.

1. For all data sets, the slopes ranged from 0.464 to 0.937.

2. Coefficients of Determination ranged from 0.61 to 0.96.

3. All slopes were statistically different from 1.0 except in two instances.

4. The 95 percent Confidence Intervals of the slopes ranged from ±0.2 to ±0.5 pH units.

5. All three sensors exhibited an apparent change in slope after the passage of Hurricane Bob. The Martek not only changed its slope but also the level. The Hydrolab had a relatively small change in slope while the Ocean Data decreased from 0.793 to 0.525. One hypothesis for this apparent anomaly is as follows. Prior to Hurricane Bob, the pH values were clustered about a 9.5 to 11.0 range, with a relatively high scatter so that a linear trend is not readily apparent. It is possible that a change in the calibration could have occurred during this period that would go unnoticed due to the small pH range. After the passage of Hurricane Bob, the pH values decreased for a period of time to as low as 7.5 so that a much larger range of data was available. The actual slope at this time would then be more readily apparent. The pH sensors were calibrated over a range of 7.0 to 10.0, the range expected to be encountered in the lake. Assuming that the LSF of the data before Hurricane Bob is an adequate representation of the actual calibration characteristics, the following fitted values of pH are obtained:

	Actual pH	
	7	10
Hydrolab	7.0	9.4
Martek (MK1)	7.5	9.7
Martek (MK2)	7.7	10.1
Ocean Data	7.3	9.7

These values seem to be consistent with the initial calibration range of 7 through 10. It thus appears that the pH sensors all underwent a deterioration in the calibration over the 41-day period. The only other explanation is that the pH sensors are in some way affected by hurricanes. After the hurricane, if it is assumed that the LSF of the post-hurricane data adequately represents the sensor calibration at that time, the following fitted values of pH are

TABLE 2. LEAST SQUARES REGRESSION ANALYSIS OF OBSERVED pH AGAINST A DEFINED STANDARD pH

Data Source	Range of pH	Summary of Least Squares Fit (LSF)				
		Slope	Intercept	R^{2*}	0.95 CI†	NDP‡
II, HL freshwater	9.0-10.0	0.503	4.462	0.83	±0.2	34
II, MK freshwater	9.0-10.0	0.666	3.496	0.79	±0.2	34
III, HL1§ freshwater	9.3-11.0	0.807	1.310	0.72	±0.4	54
III, MK1# freshwater	9.5-11.0	0.732	2.364	0.72	±0.3	35
III, MK2# freshwater	9.3-10.5	0.781	2.239	0.74	±0.5	12
III, MK3# freshwater	9.6-10.5	0.657	2.692	0.97	±0.3	4
III, MK4# freshwater	7.5-11.0	0.464	3.839	0.89	±0.4	36
III, OD1** freshwater	9.5-11.0	0.793	1.767	0.61	±0.5	49
III, OD2** freshwater	7.5-11.0	0.525	4.544	0.86	±0.5	38
III, HL2§ freshwater	7.5-11.0	0.937	-0.053	0.98	±0.5	38

* Coefficient of Determination, R^2

† 95 percent Confidence Interval of the slope

‡ Number of Data Points

§ The Hydrolab also appeared to change its slope after Hurricane Bob. HL1 is for data prior to Hurricane Bob and HL2 is for data after Hurricane Bob.

\# The Martek pH parameter exhibited an apparent correlation to the occurrence of rainfall. The MK1 data is prior to the removal of the Martek package after the first 14 days. The MK2 data is for the period from redeployment at 15 days until the occurence of a light rainfall after a very dry June. The MK3 data is for the period after the rainfall until the onset of Hurricane Bob which was accompanied by heavy rainfall. The MK4 data is for the period after the passage of Hurricane Bob until the end of the test. The pH sensor was recalibrated prior to redeployment.

** The Ocean Data also appeared to change its slope after Hurricane Bob. The OD1 data is for data prior to Hurricane Bob and the OD2 is for data after Hurricane Bob.

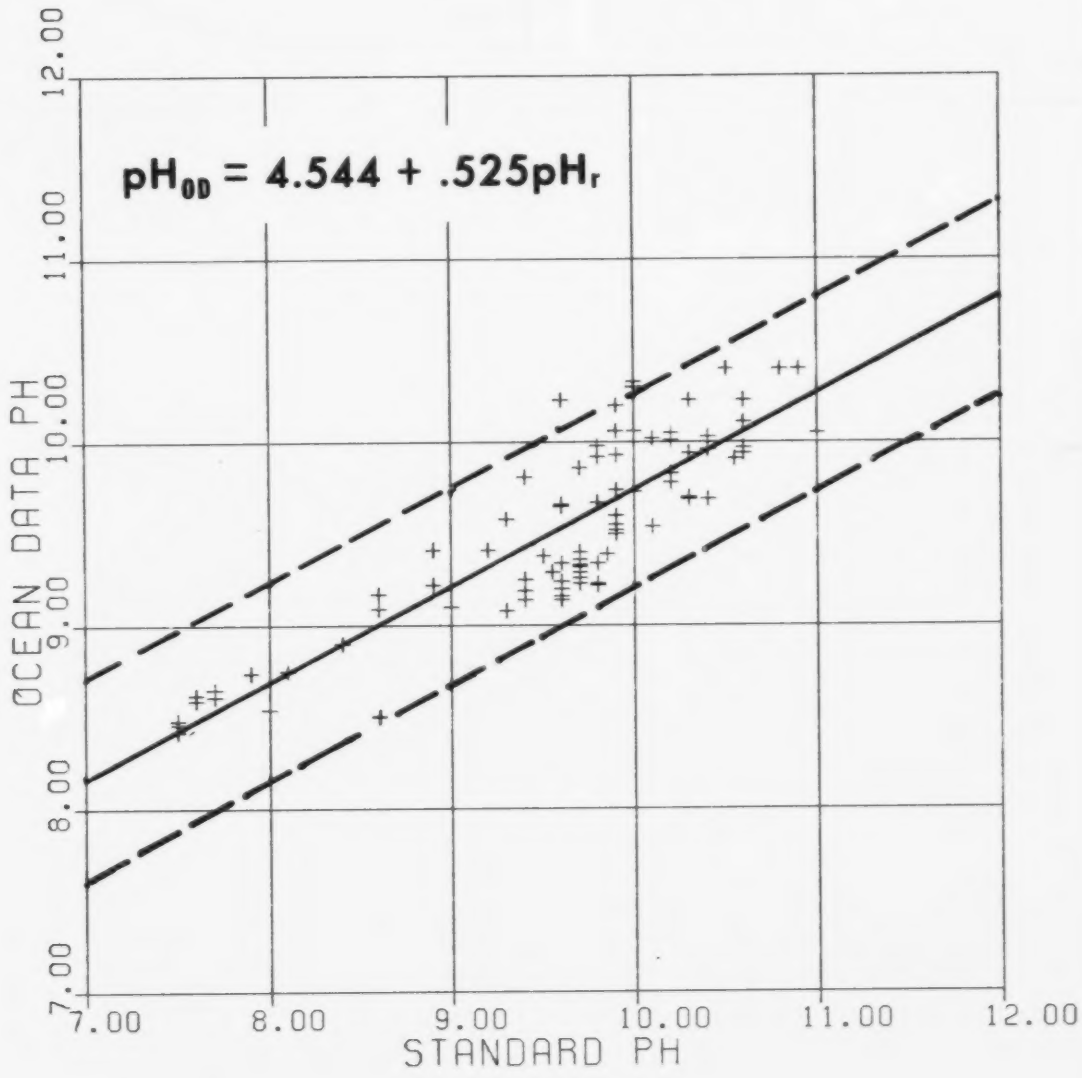

Figure 16. Ocean Data pH vs. standard pH, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean pH values for the Ocean Data.)

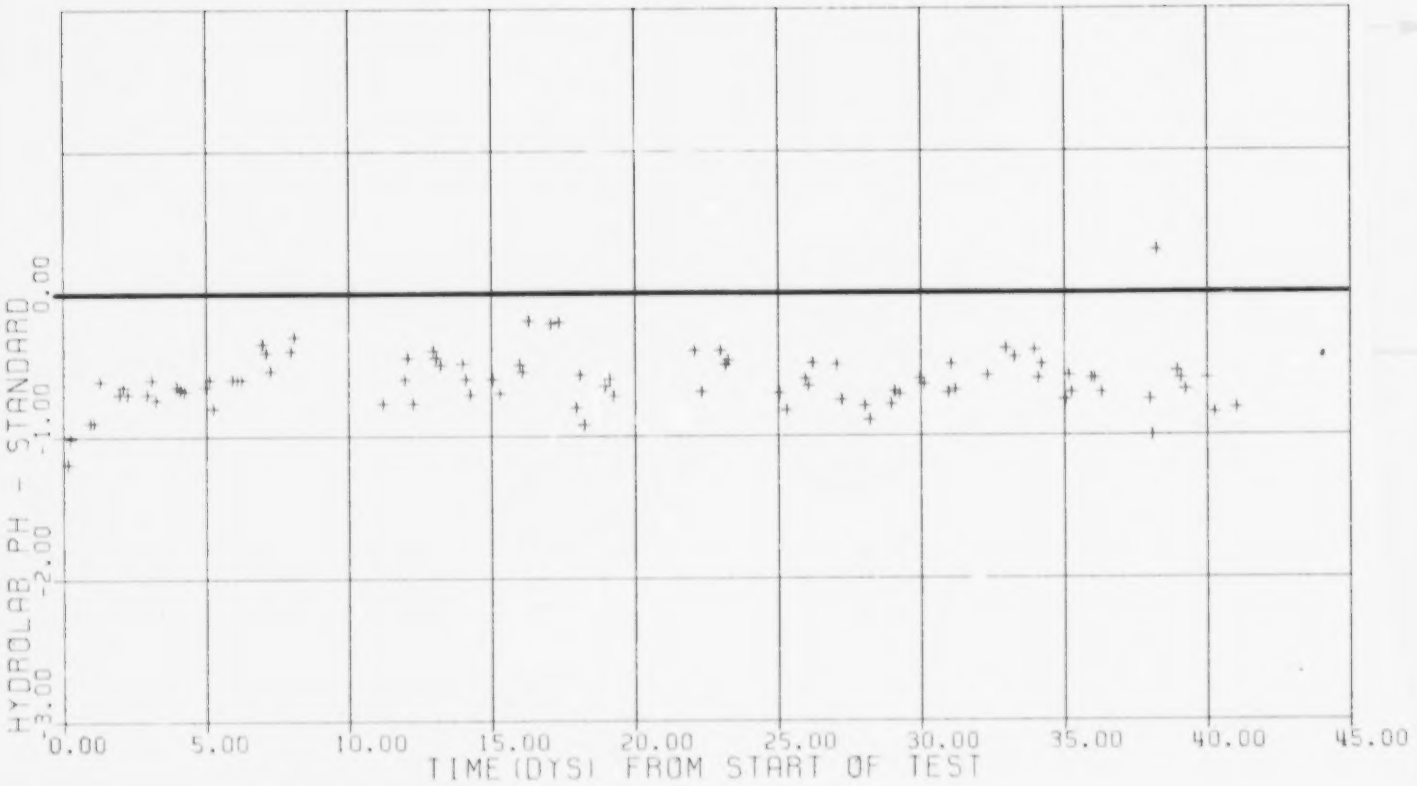

Figure 17. Ocean Data pH vs. time, Data Set III.

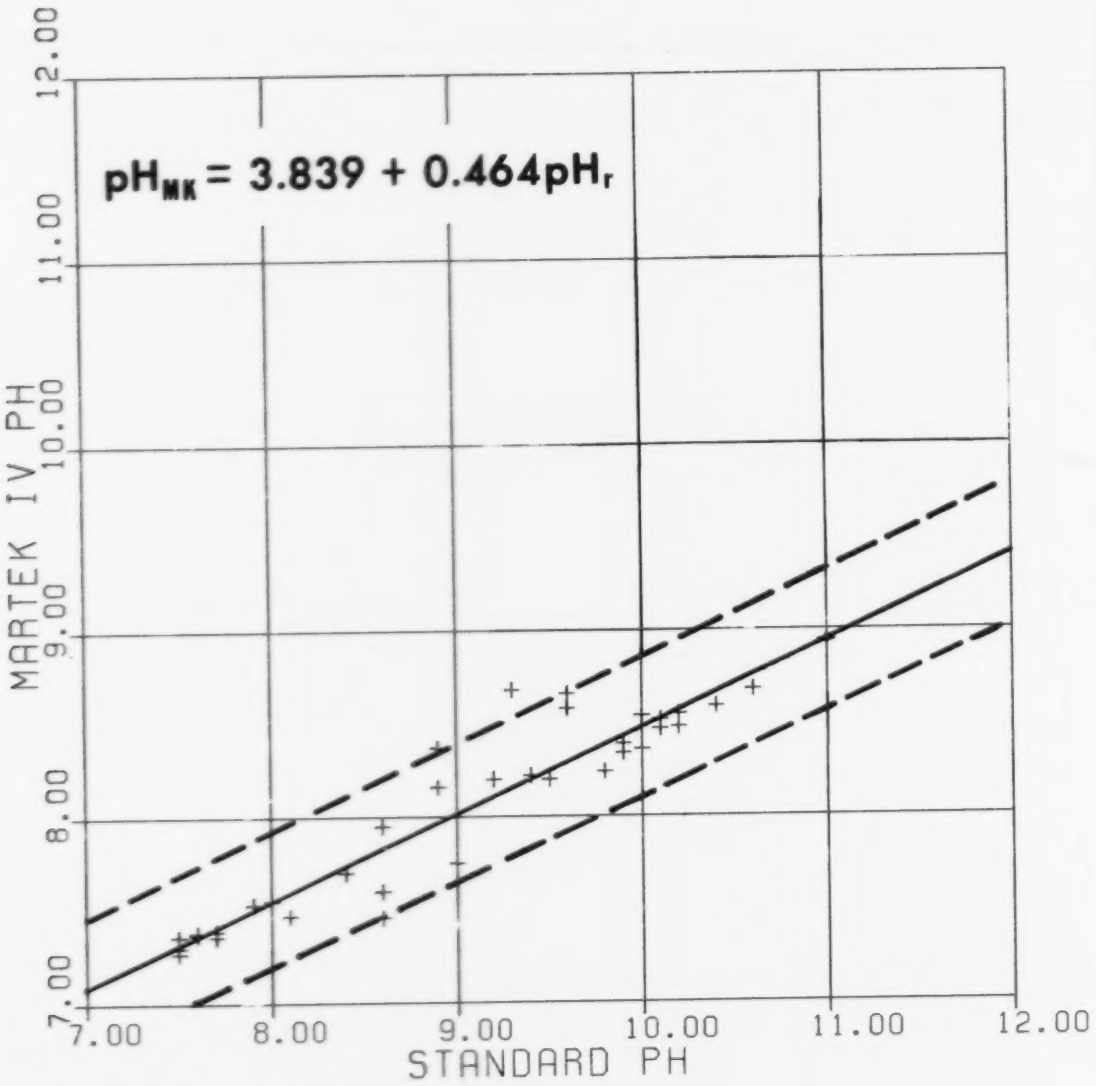

Figure 18. Martek IV pH vs. standard pH, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean pH values for the Martek IV. Values above 9 pH units on the y axis were not used in determining the regression equation.)

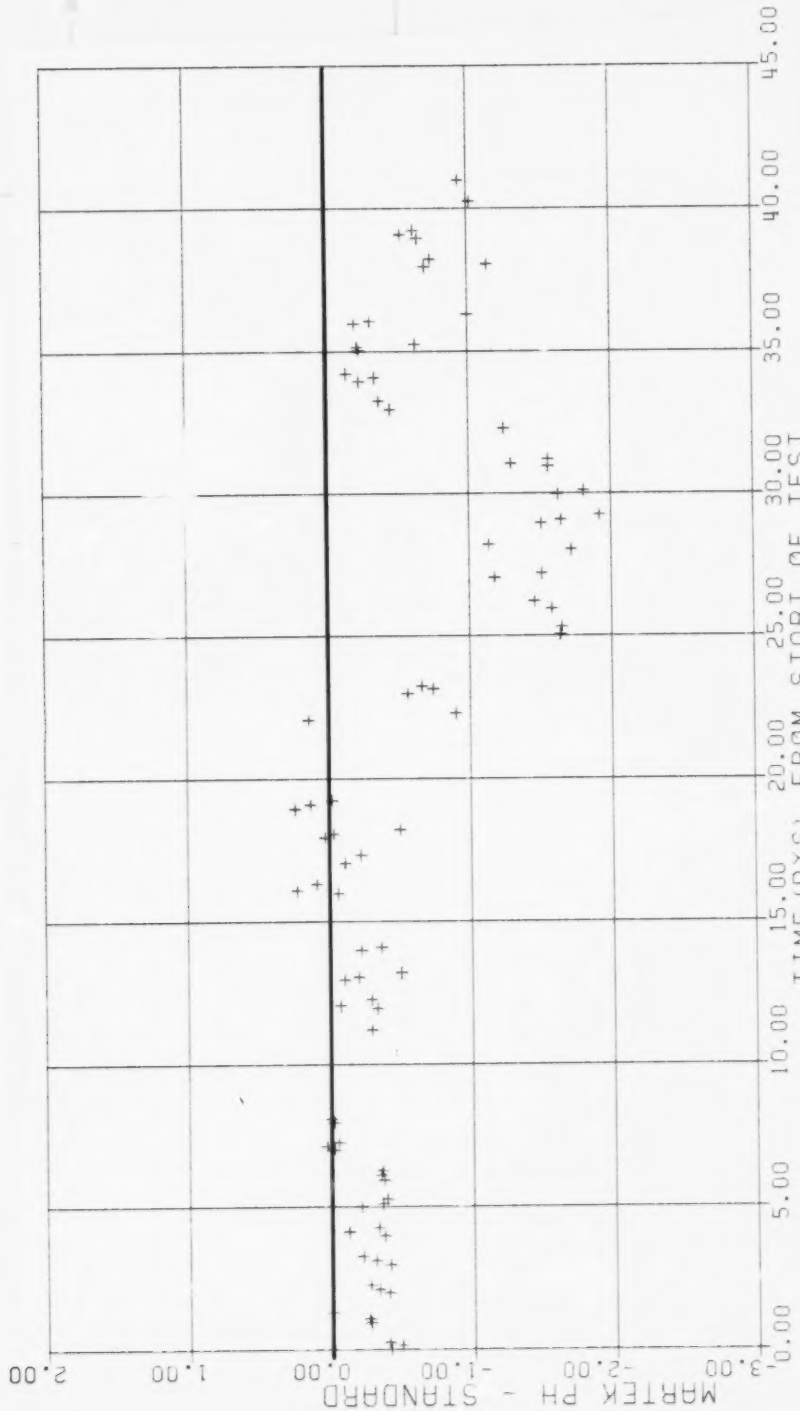

Figure 19. Martek IV pH vs. time, Data Set III.

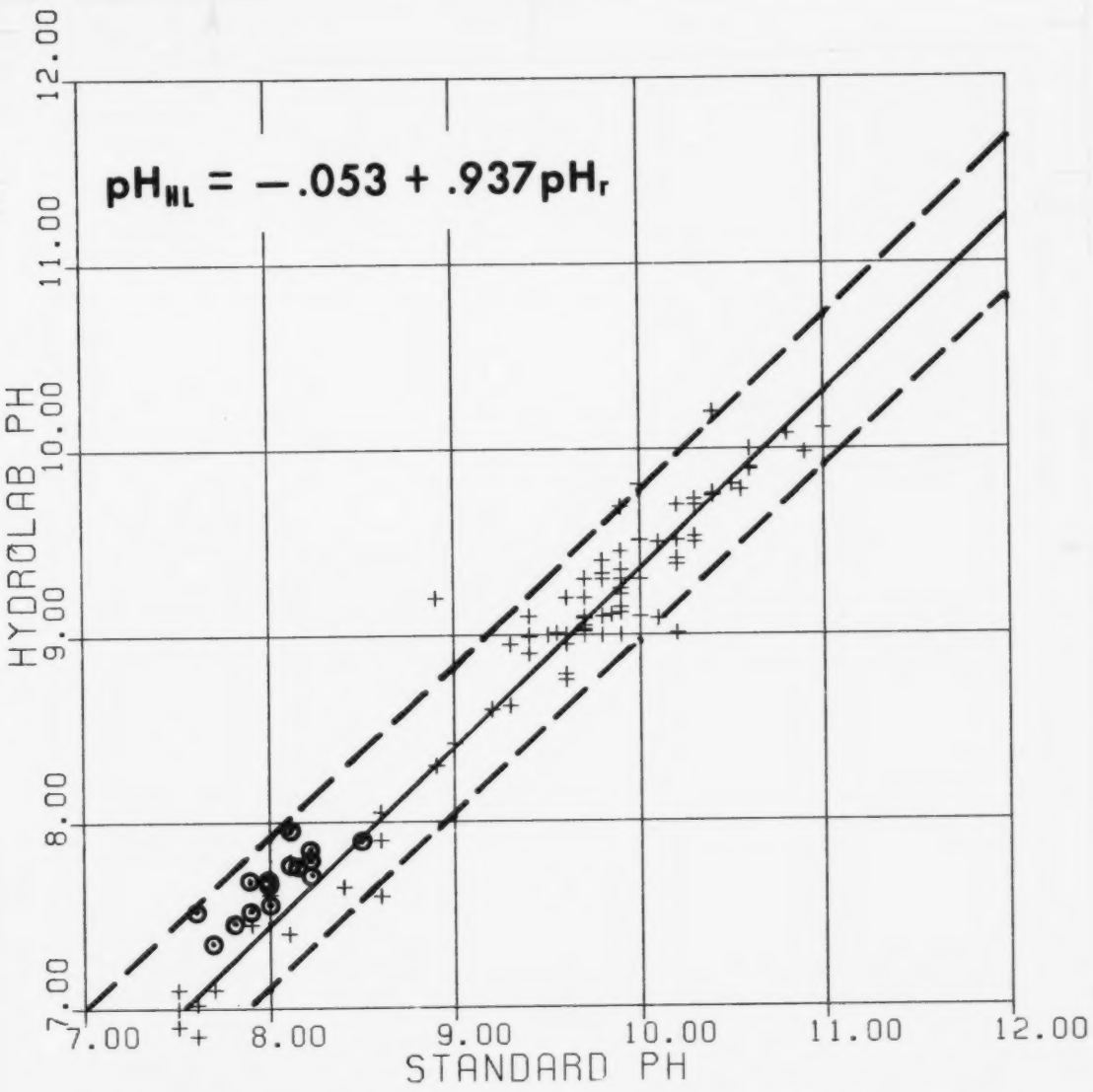

Figure 20. Hydrolab pH vs. standard pH, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean pH values for the Hydrolab.)

obtained for actual pH values of 7 and 10:

	Actual pH	
	7	10
Hydrolab	6.5	9.3
Martek (MKIV)	7.1	8.5
Ocean Data	8.2	9.8

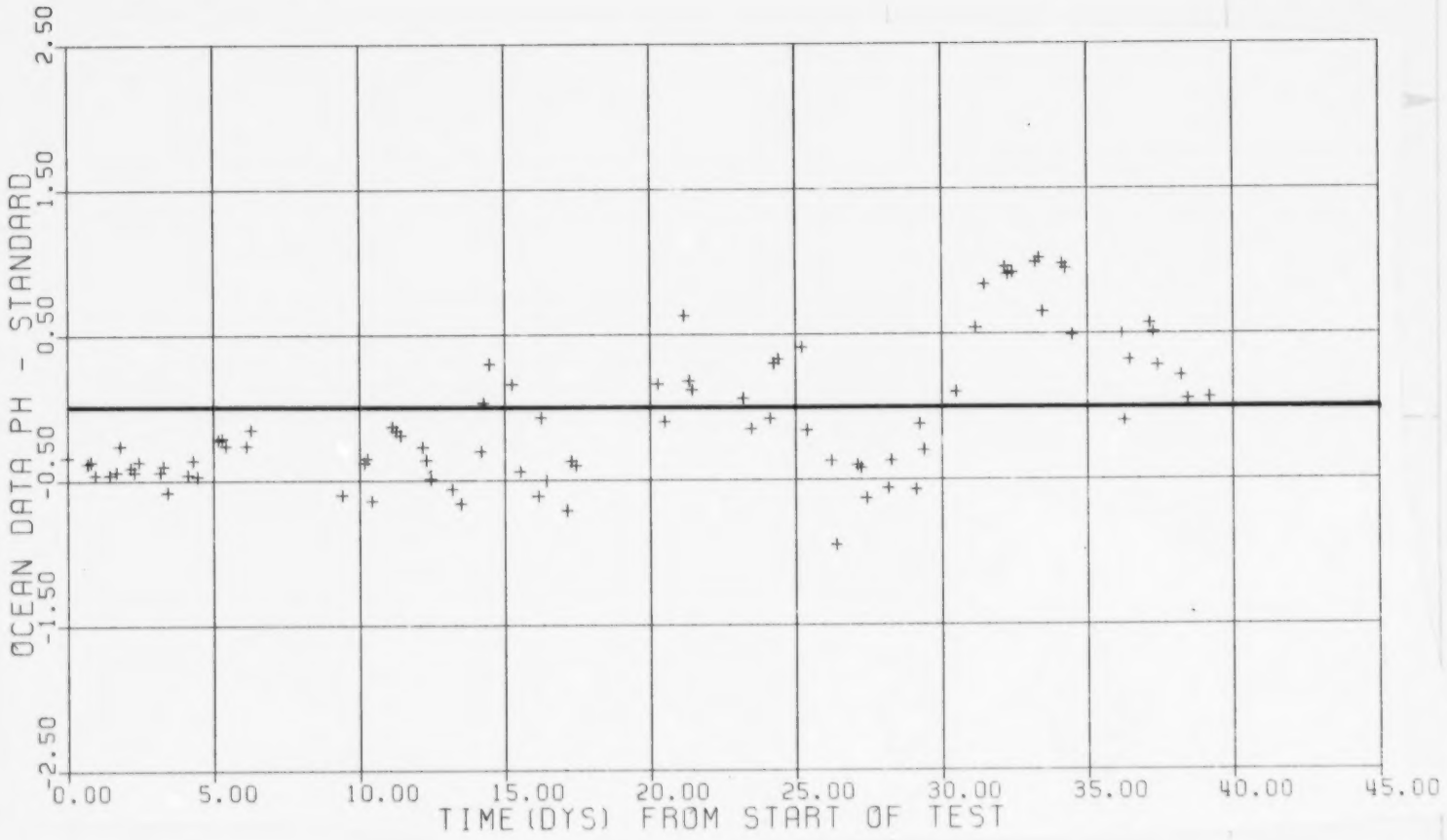

Figure 21. Hydrolab pH vs. time, Data Set III.

After the field tests, the probes were cleaned and tested in the laboratory with the following results.

Hydrolab (after cleaning)	7.1	8.9
Martek (cleaning not required)	7.4	8.5
Ocean Data (after cleaning)	7.3	10.6

These data suggest that the Hydrolab pH sensor did not drift significantly over the range of calibration since the upper and lower values are all within 0.5 pH units of each other. If any drift did occur it was probably at the lower set point. The Martek lower end point remained fairly constant, but the upper end appeared to be affected by time from initial calibration since biofouling of the Martek sensors was effectively eliminated. The Ocean Data upper end point was fairly stable, the upper end increasing after cleaning, but the lower end point seemed to be affected by fouling (increasing from 7.3 to 8.2) but recovered after cleaning. Thus the OD seems to be fairly stable if kept clean, but is affected by fouling.

CONDUCTIVITY

Data analysis for the conductivity sensors from Data Sets I, II and III is presented in Table 3 and plots from Data Set III are given in Figures 22 through 25. Specific observations are:

1. The conductivity measurements were by far the most erratic of the parameters measured.
2. No conductivity measurements for the Ocean Data were obtained because of an inability to calibrate the sensor.
3. Slopes ranged from -0.698 to 1.112.
4. Coefficients of Determination ranged from 0.01 to 0.75.
5. The 95 percent Confidence Intervals of the slope ranged from ±10 to ±120 in fresh water, ±1125 in brackish, ±1300 in seawater.
6. The Hydrolab tended to saturate at the lower end of the conductivity range in the brackish and seawater data sets. For the range of conductivities in which a linear trend was evident, the HL slopes were 0.531 and 0.556 with 95 percent Confidence Intervals equal to 10 percent and 3 percent of the average conductivity respectively for brackish and seawater.
7. In freshwater, the uncertainty ranged from 15 to 24 to 93 percent of the average conductivity for the Hydrolab.
8. The Martek uncertainty in freshwater ranged from 5 to 19 to 37 percent.
9. The significant deviation of the slopes from 1.0 suggests a similar situation as was hypothesized for the pH sensors. No attempt to further investigate this parameter was made due to time limitations.

TABLE 3. LEAST SQUARES REGRESSION ANALYSIS OF OBSERVED CONDUCTIVITY AGAINST A DEFINED STANDARD CONDUCTIVITY

Data Source	Range of Conductivity*	Summary of Least Squares Fit (LSF)				
		Slope	Intercept*	R^2†	0.95 CI‡	NDP§
I, HL freshwater	550-1000	1.021	-20	0.71	±120	69
I, HL1B# brackish	5500-8500	0.071	4679	0.04	±600	28
I, HL2B# brackish	8500-14000	0.531	922	0.55	±1125	50
I, HL1S** seawater	31500-38000	0.251	24414	0.12	±3600	21
I, HL2S** seawater	38000-45000	0.556	13394	0.75	±1300	41
II, HL freshwater	95-121	-0.698	198	0.01	±100	36
II, MK freshwater	95-121	1.799	137	0.49	±40	36
III, HL freshwater	150-270	0.767	20	0.37	±50	96
III, MK1†† freshwater	150-270	0.241	53	0.15	±10	42
III, MK2†† freshwater	150-270	1.112	-13	0.64	±40	41

* Conductivities in micromho/cm
† Coefficient of Determination, R^2
‡ 95 percent Confidence Interval of the slope
§ Number of Data Points
\# The conductivity as indicated by the sensor was saturated over the indicated range. The HL1B data are for standard conductivities in the range of 5500 to 8500 and the HL2B data are for standard conductivities in the range 8500 to 14000
** As for the brackish water data, the HL1S data are for conductivities in the range 31500 to 38000, and the HL2S data are for conductivities in the range 38000 to 45000.
†† The Martek package was removed after fourteen days exposure. The MK1 data is for the first fourteen days data. After checking the dissolved oxygen circuitry, the conductivity circuit was recalibrated and the package redeployed. The conductivity as indicated by the sensor was very erratic for a period of 5 days, then settled down. The MK2 data is for the period after the sensor stabilized and the end of the test.

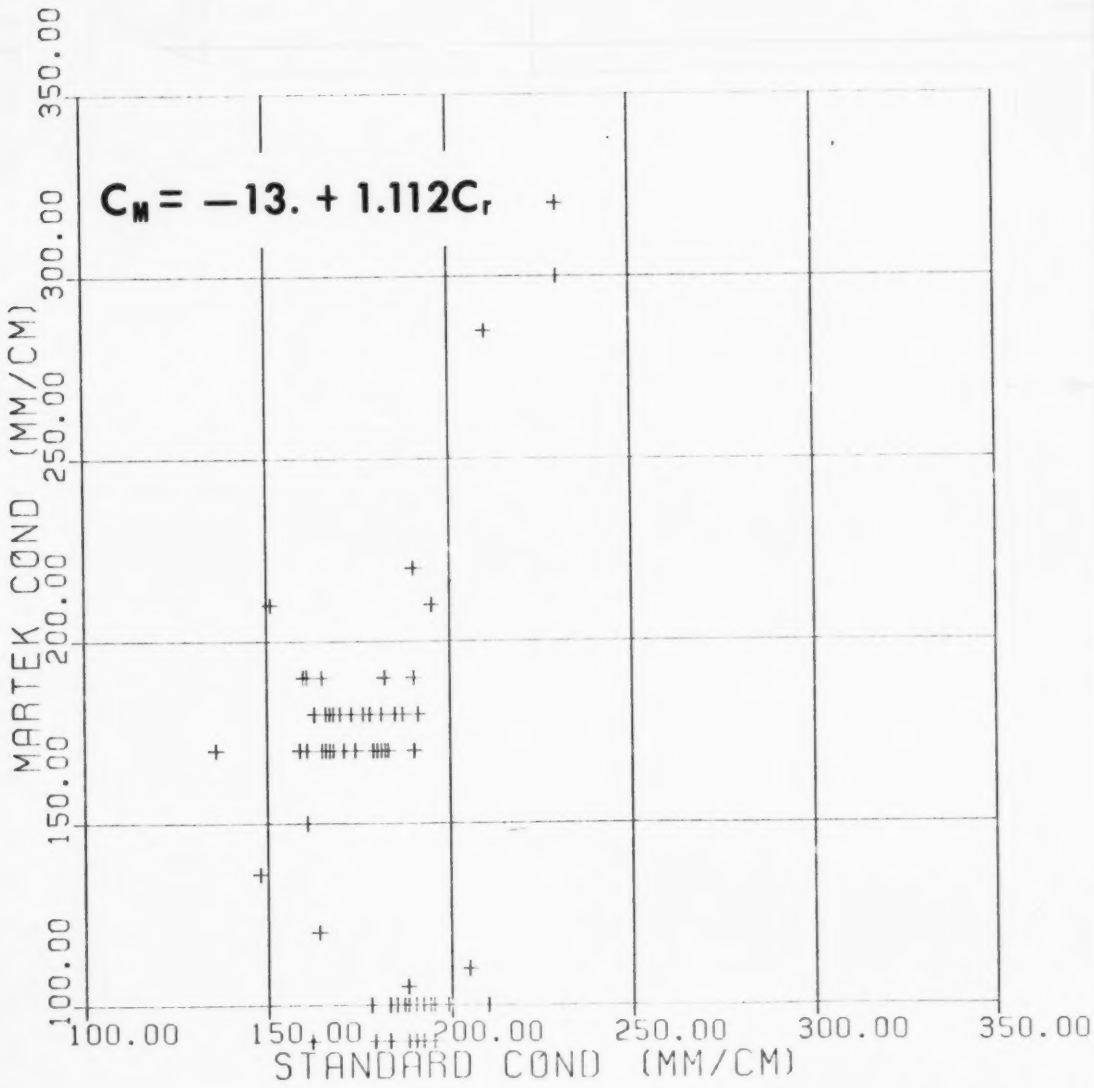

Figure 22. Martek conductivity vs. standard conductivity, Data Set III.

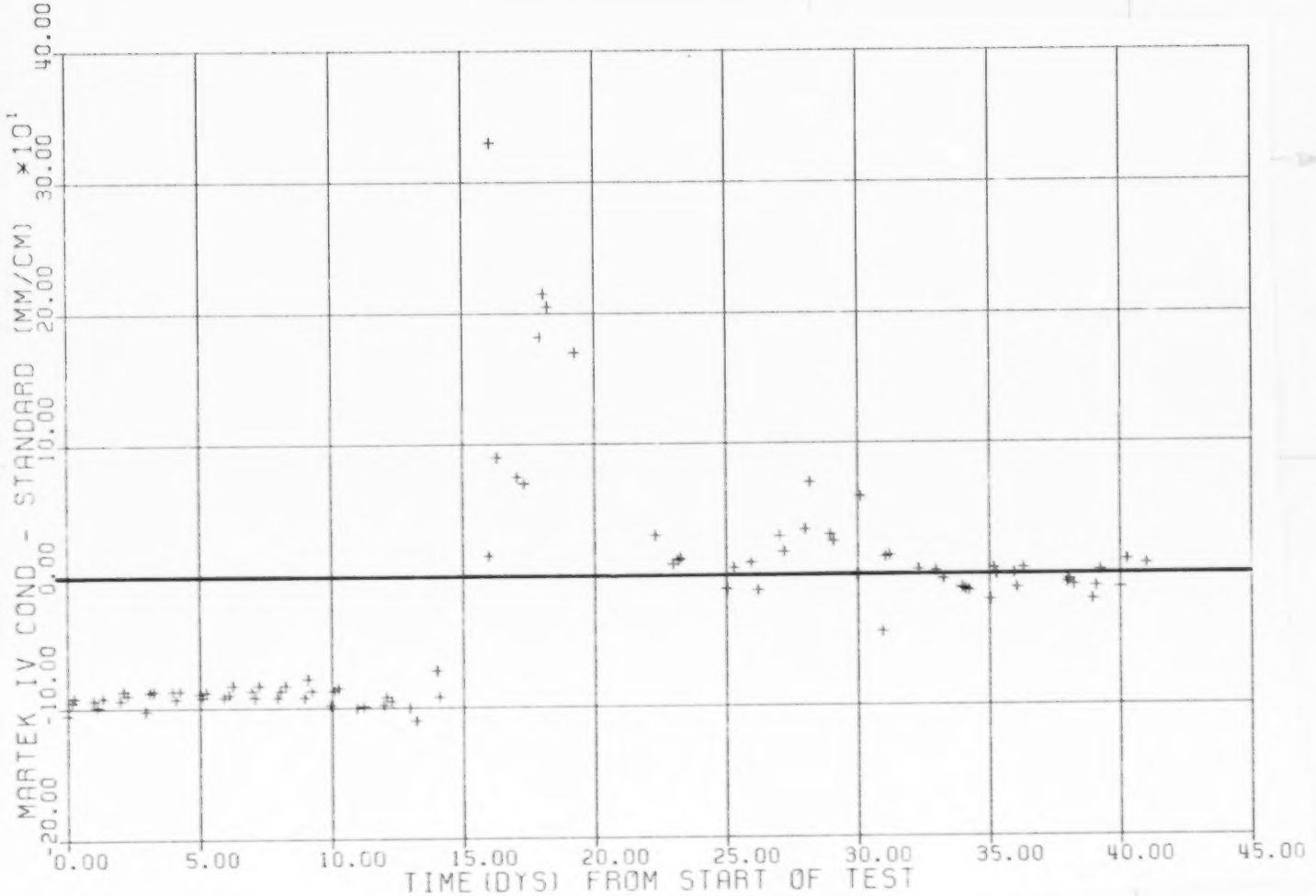

Figure 23. Martek conductivity vs. time, Data Set III.

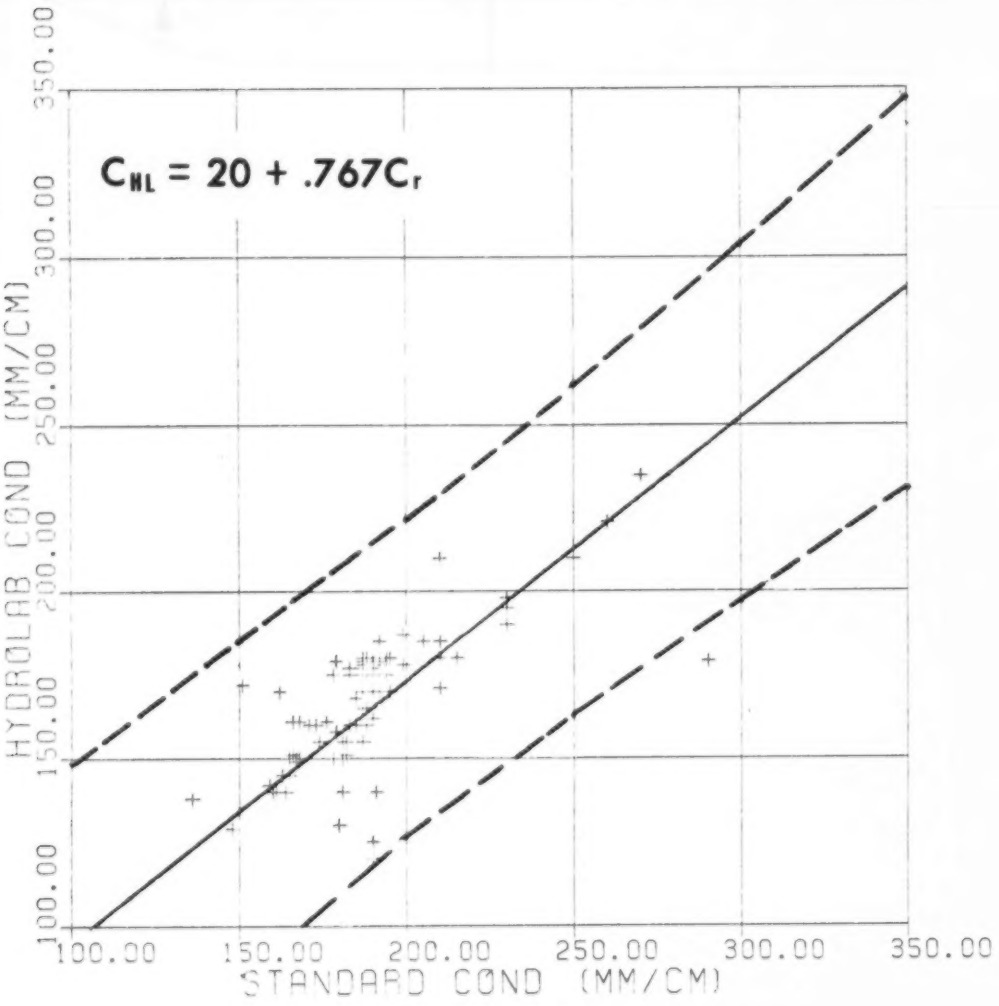

Figure 24. Hydrolab conductivity vs. standard conductivity, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean conductivity values for the Hydrolab.)

DISSOLVED OXYGEN

Table 4 presents an analysis of data from Data Sets I, II, and III and for DO measurements, and Figures 26 through 29 are plots of the data obtained in Data Set III. Observations about the data are as follows.

1. The Hydrolab and Ocean Data DO sensors performed well in that the slopes ranged from 0.954 to 1.073 and Coefficients of Determination ranged from 0.88 to 0.97.

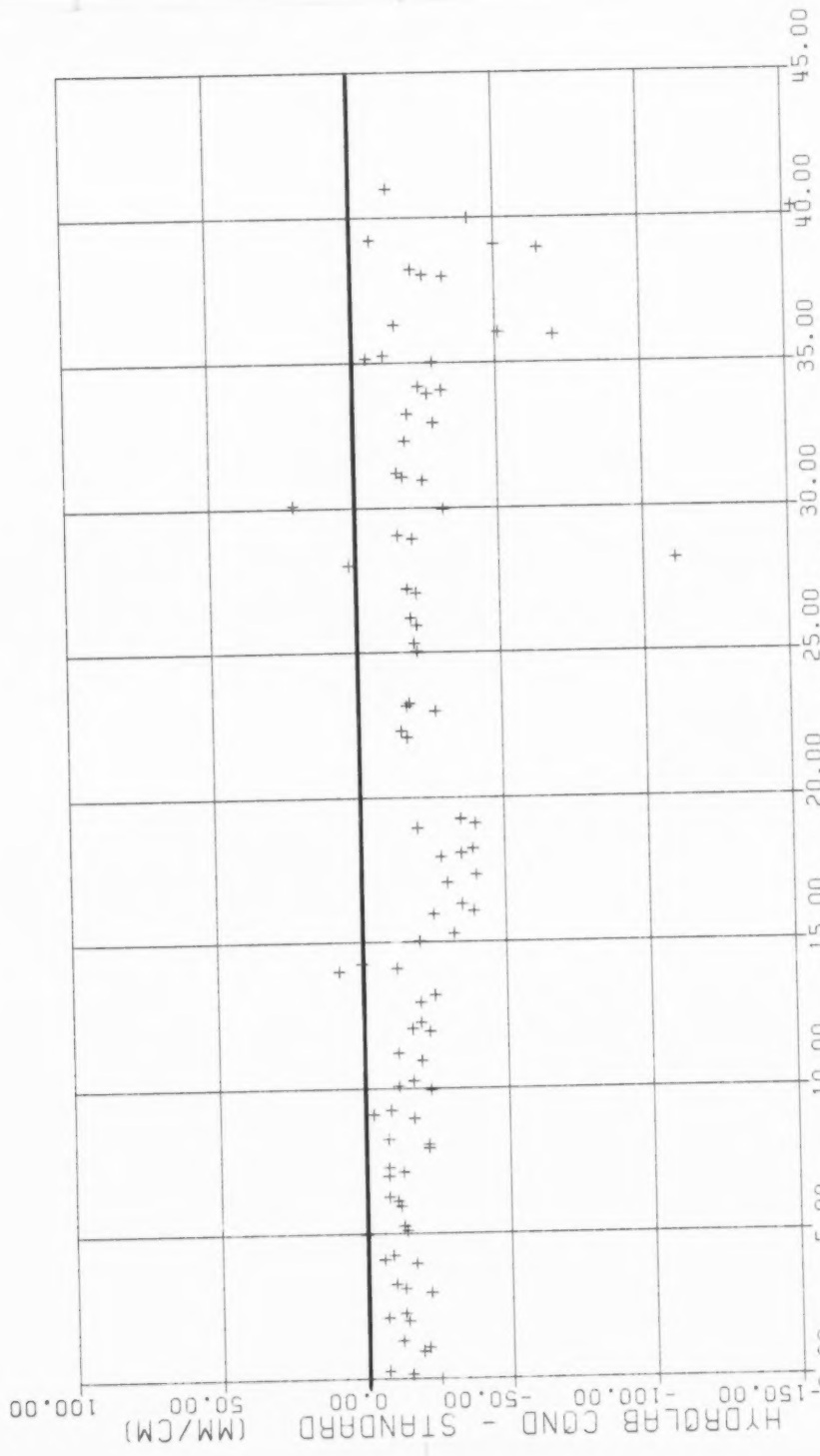

Figure 25. Hydrolab conductivity vs. time, Data Set III.

TABLE 4. LEAST SQUARES REGRESSION ANALYSIS OF OBSERVED DISSOLVED OXYGEN AGAINST A DEFINED STANDARD DISSOLVED OXYGEN

Data Source	Range of DO (ppm)	Summary of Least Squares Fit (LSF)				
		Slope	Intercept (DO ppm)	R^2*	0.95 CI†	NDP‡
I, HL§ freshwater	2-12	0.954	0.105	0.95	±1.15	37
I, HL§ brackish	3-9	1.073	-0.411	0.88	±1.05	37
I, HL§ seawater	5-9	1.051	-0.490	0.89	±0.80	30
II, HL freshwater	7-18	0.961	0.735	0.90	±1.70	35
II, MK freshwater	7-18	0.666	4.782	0.62	±2.75	36
III, HL freshwater	0-20	0.966	-0.296	0.97	±1.95	74
III, OD# freshwater	0-17	1.048	-0.124	0.96	±2.10	67

* Coefficient of Determination, R^2

† 95 percent Confidence Interval of the slope

‡ Number of Data Points

§ The circulator failed before the test run was completed. The data presented were taken before the circulator failed.

\# The Ocean Data DO sensor saturated at DO greater than 17 ppm. The data presented are for those values of standard DO less than 17 ppm.

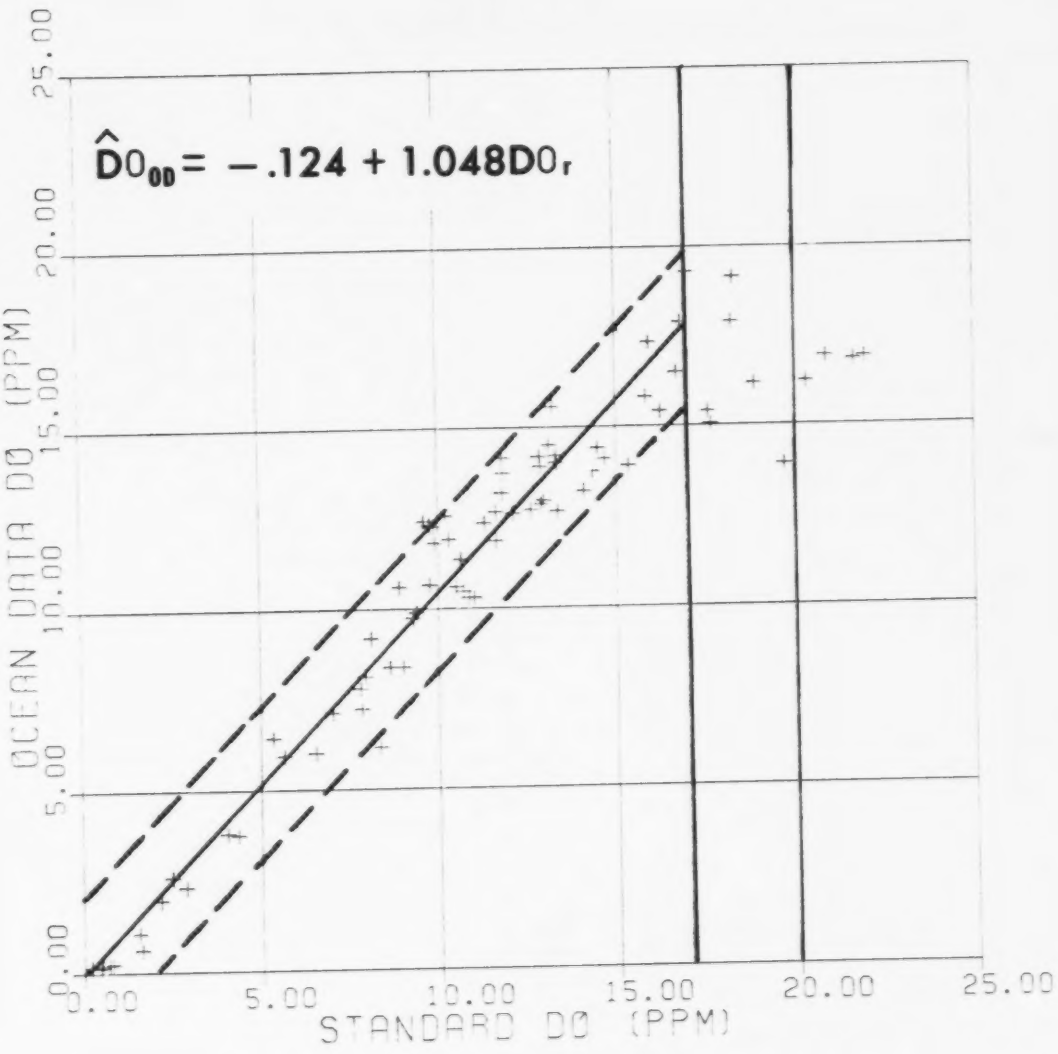

Figure 26. Ocean Data DO vs. standard DO, Data Set III. (Values above 15.4 DO units on the x axis were not used in determining the regression equation. The dashed lines are the 95 percent confidence interval for the prediction of mean DO values for the Ocean Data.)

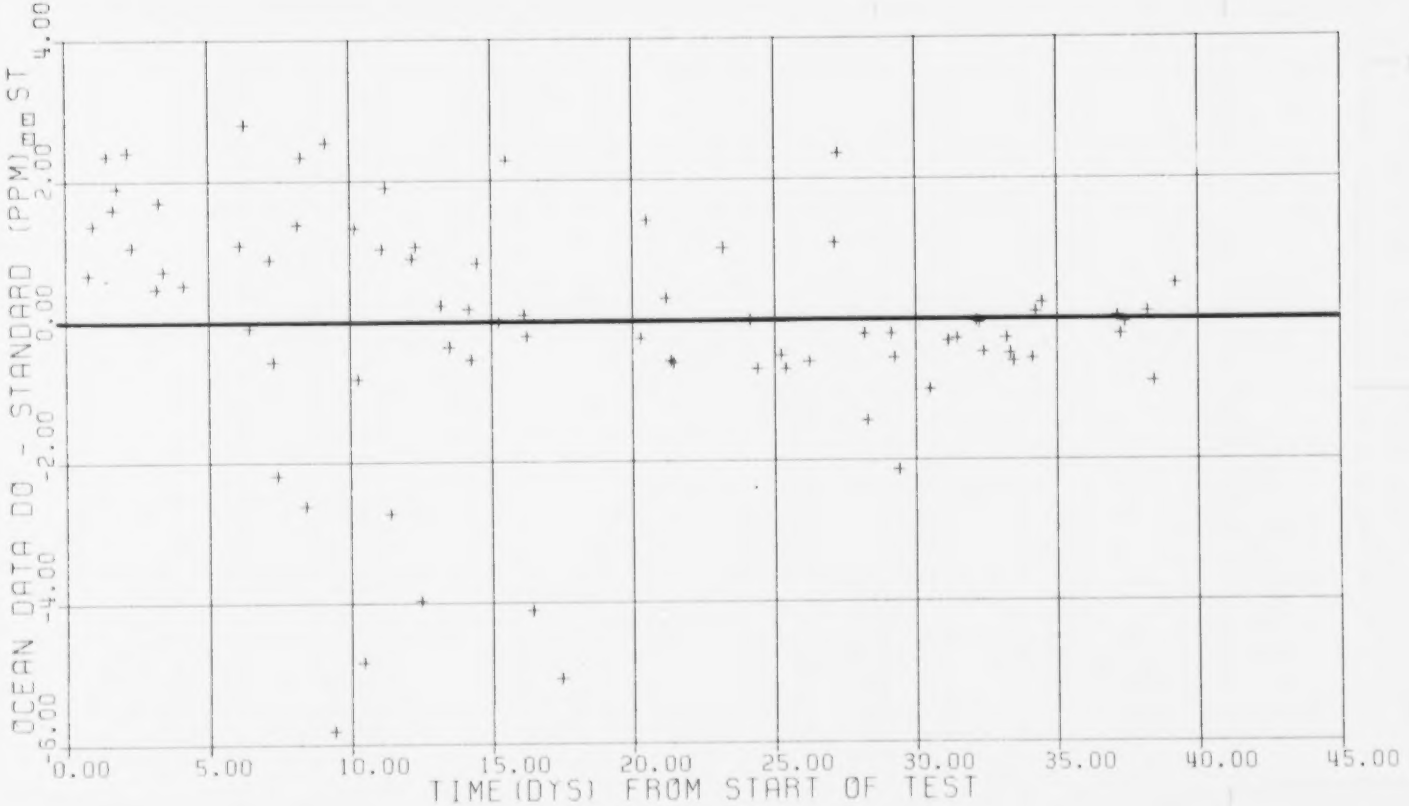

Figure 27. Ocean Data DO vs. time, Data Set III.

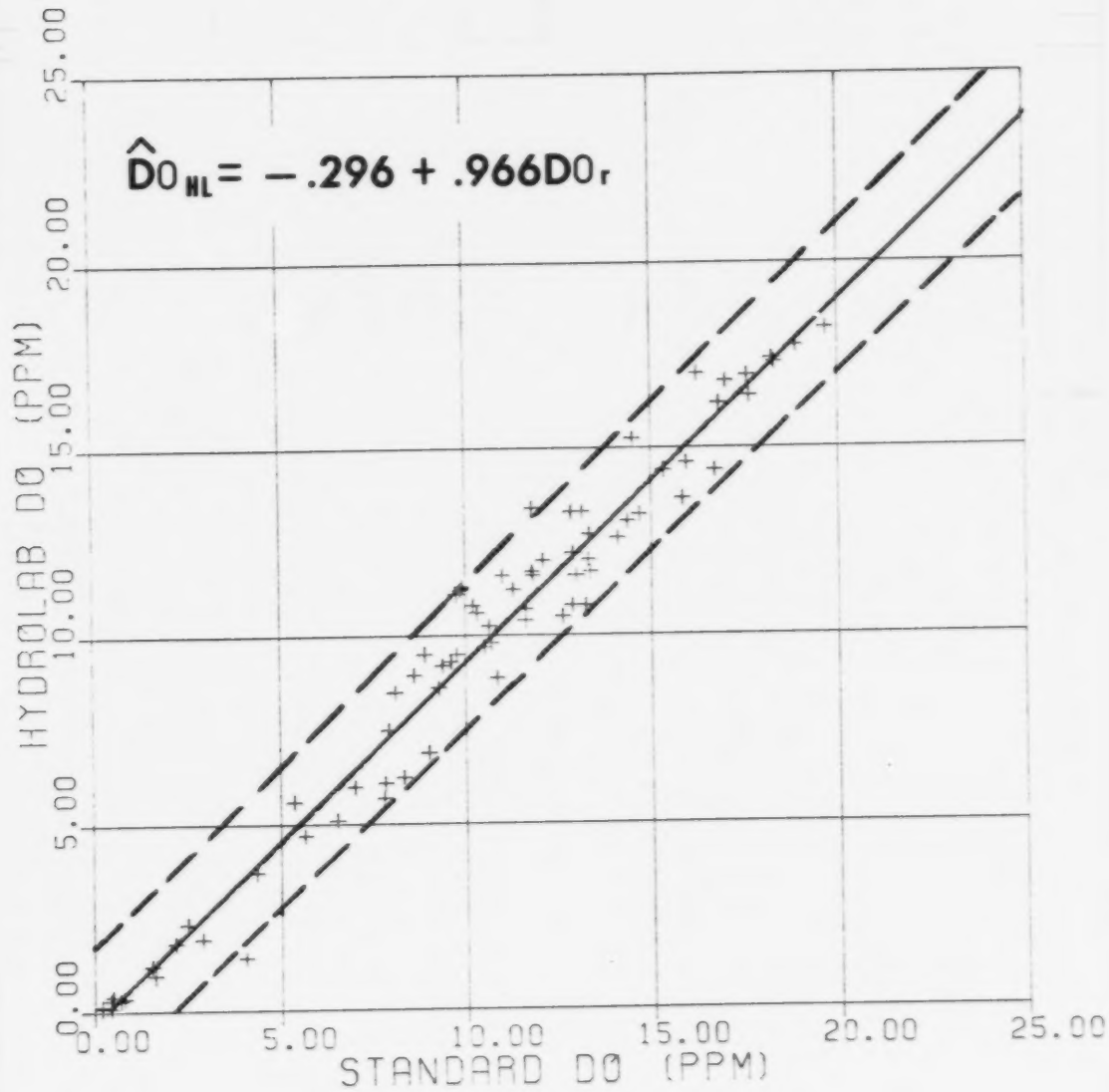

Figure 28. Hydrolab DO vs. standard DO, Data Set III. (The dashed lines are the 95 percent confidence interval for the prediction of mean DO values for the Hydrolab.)

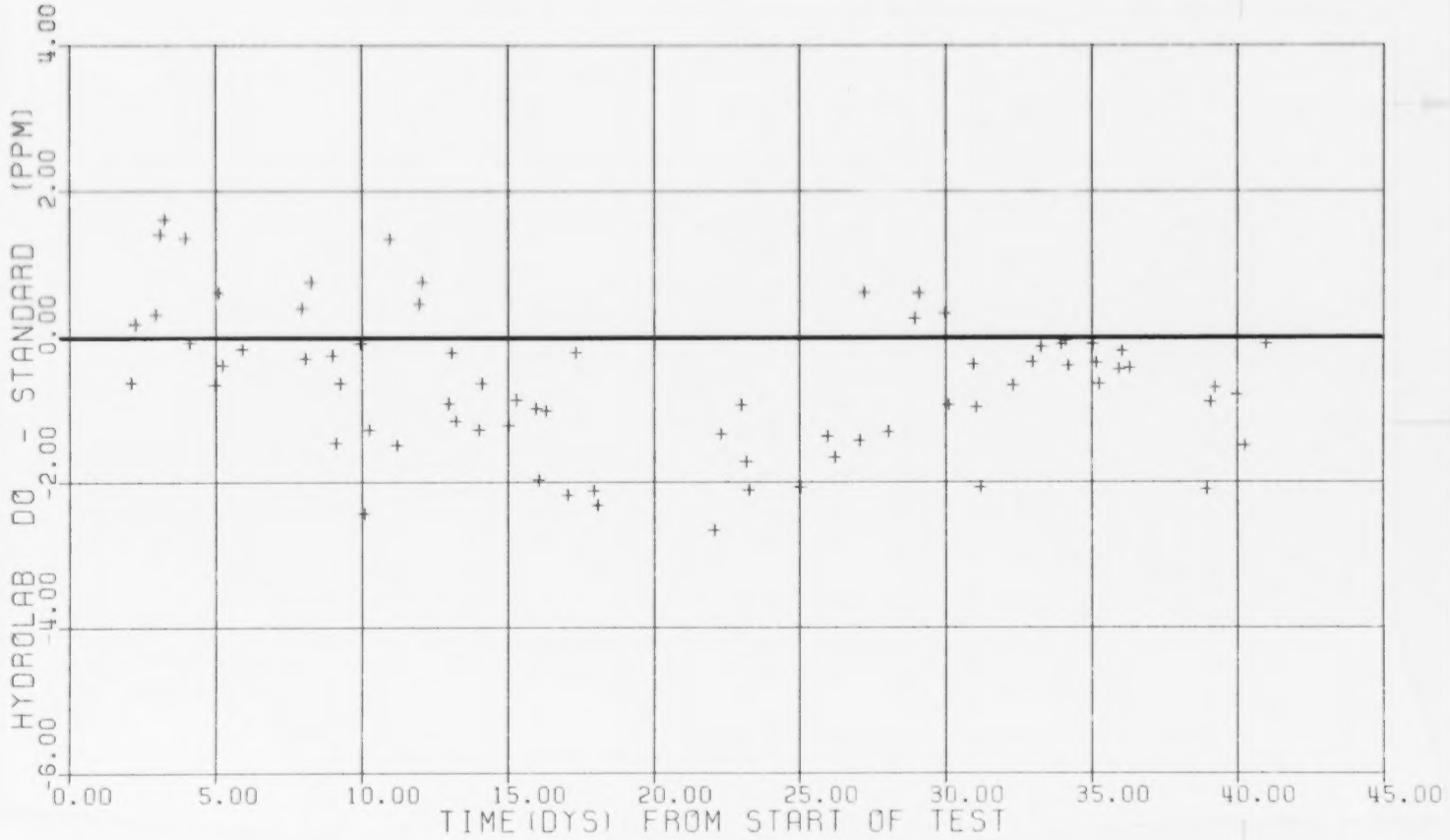

Figure 29. Hydrolab DO vs. time, Data Set III.

2. All slopes for the HL and OD were not statistically different from 1.0 at the 5 percent probability level.

3. The 95 percent Confidence Interval for the HL ranged from ±1.05 to ±1.95.

4. The 95 percent Confidence Interval for the OD was ±2.10 for DO values from 0 to 17. At values of DO greater than 17, the OD sensor appeared to saturate and level out.

5. The Martek DO sensor gave very erratic data for the the 41-day test and was not deemed reliable enough to perform an analysis.

6. The Martek data for Data Set II give a slope of 0.666, coefficient of determination of 0.62 and an uncertainty of ±2.75. This slope is statistically less than 1.0.

7. The Martek DO sensor after 41 days exposure, protected by the enclosure and antifouling paint, gave a slope of 0.683, R^2 of 0.943 and an uncertainty of ±1.4 ppm (Data Set IV).

CALIBRATION

The instruments were calibrated according to the manufacturer's instructions. The calibration procedures call for calibration setpoints at most, 2 points, preferably over the range of parameter values expected in the field measurements.

In the 6-week field test discussed in this report, the pH range from 7.5 to 11 and the dissolved oxygen (DO) ranged from 0 ppm to 20 ppm. Due to the very large range of variation of the pH and DO, the calibration procedures should be changed to allow additional setpoints. This would require changes in the electronic circuitry to permit additional setpoints to be added. This would result in greater stability over the entire range of parameter variation. Therefore, the drift of any one setpoint would not affect the entire calibration curve.

Due to the inherent variation of the probe readings, it would be desirable to take several probe measurements of a given parameter over a period of time after the initial calibration, holding the actual parameter value constant. The average of the resultant distribution of probe readings should then agree with the actual value of the parameter being measured. If it does not, then the difference between the actual value and the probe average reading should be added to the current probe reading and the circuitry readjusted to reflect the new calibration. This procedure may be repeated if necessary until the average of the indicated probe readings is equal to the actual value of the parameter being measured. This procedure would eliminate any calibration bias due to a one-time calibration adjustment.

SUMMARY OF DATA FOR ALL PARAMETERS

Table 5 presents a summary of statistical tests for null hypothesis for each parameter and each data set. Whether or not the data were statistically acceptable is shown.

Table 6 presents the results obtained from Data Set IV, the data taken after field tests were completed and the probes cleaned. The tests were accomplished in the instrumentation laboratory at LSU under controlled conditions.

TABLE 5. SUMMARY OF STATISTICAL TESTS FOR NULL HYPOTHESIS (H_o: b = 1)

Data Source	Parameter	b*	SD of b†	t‡	Accepts§	Rejects§
I, HL freshwater	T	0.934	0.059	-1.12	*	
I, HL brackish	T	0.991	0.089	-0.10	*	
I, HL seawater	T	1.065	0.025	2.60		*
II, HL freshwater	T	0.995	0.048	0.10	*	
II, MK freshwater	T	1.013	0.026	0.50	*	
III, HL freshwater	T	1.017	0.018	0.94	*	
III, MK* freshwater	T	0.955	0.025	-1.80	*	
III, MK† freshwater	T	0.902	0.018	-5.40		*
III, OD freshwater	T	0.986	0.033	-0.42	*	
II, HL freshwater	pH	0.503	0.061	-8.15		*
II, MK freshwater	pH	0.666	0.061	-5.50		*
III, HL* freshwater	pH	0.807	0.058	-3.33		*
III, MK* freshwater	pH	0.732	0.079	-3.40		*
III, MK† freshwater	pH	0.781	0.145	-1.51	*	

(continued)

TABLE 5. (Continued)

Data Source	Parameter	b*	SD of b†	t‡	Accepts§	Rejects§
III, MK‡ freshwater	pH	0.657	0.016	-21.4		*
III, MK§ freshwater	pH	0.464	0.028	-19.1		*
III, OD* freshwater	pH	0.793	0.067	-3.09		*
III, OD freshwater	pH	0.525	0.035	-13.47		*
III, HL† freshwater	pH	0.937	0.040	-1.58	*	
I, HL freshwater	C	1.021	0.079	0.27	*	
I, HL2B brackish	C	0.531	0.070	-6.70		*
I, HL2S seawater	C	0.556	0.052	-8.54		*
II, HL freshwater	C	-0.698	1.360	1.25	*	
II, MK freshwater	C	1.799	0.550	1.45	*	
III, HL freshwater	C	0.767	0.100	-2.26		*
III, MK* freshwater	C	0.241	0.093	-8.16		*
III, MK† freshwater	C	1.112	0.134	0.84	*	

(continued)

TABLE 5. (Continued)

Data Source	Parameter	b*	SD of b†	t‡	Accept§	Reject§
I, HL freshwater	DO	0.954	0.039	-1.18	*	
I, HL brackish	DO	1.073	0.068	1.07	*	
I, HL seawater	DO	1.051	0.070	0.71	*	
II, HL freshwater	DO	0.961	0.057	-0.68	*	
II, MK freshwater	DO	0.666	0.090	-3.71		*
III, HL freshwater	DO	0.966	0.019	-1.70	*	
III, OD freshwater	DO	1.048	0.027	1.78	*	

* b = Slope of Least Squares Fitted curve

† SD of b = Standard deviation of slope

‡ $t = \frac{b - 1.0}{SD \text{ of } B}$

§ Accept or reject at 0.05 probability level

TABLE 6. DATA SET IV, CALIBRATION CHECK OF PROBES AFTER CLEANING

Probe	Parameter	Slope	Intercept	SD of b	t	Accept*	Reject*	0.95 CI	NDP
HL	DO	0.810	0.477	0.045	4.22		*	0.9	17
OD	DO	0.928	0.927	0.052	1.38	*		1.0	17
MK	DO	0.683	0.030	0.085	3.73		*	1.4	10
HL	pH	0.615	2.742	0.113	3.407		*	0.3	17
OD	pH	0.809	1.076	0.140	1.364	*		0.3	16
MK	pH	0.381	4.689	0.093	6.656		*	0.2	15

* Accept or reject at 0.05 probability level.

(Temperature and conductivity remained essentially constant during this laboratory test.)

SECTION 7

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